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### **► To cite this version:**

R. Lucrecia López Steinmetz, Stefano Salvi, M. Gabriela García, Didier Béziat, Gabriela Franco, et al.. Northern Puna Plateau-scale survey of Li brine-type deposits in the Andes of NW Argentina. *Journal of Geochemical Exploration*, 2018, 190 (2), pp.26-38. <10.1016/j.jgexplo.2018.02.013>. <hal-02363093>

**HAL Id: hal-02363093**

**<https://hal.science/hal-02363093v1>**

Submitted on 6 Nov 2020

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# Northern Puna Plateau-scale survey of Li brine-type deposits in the Andes of NW Argentina

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## Abstract

Salars of the Andean Plateau in the Central Andes are the largest lithium deposits on Earth. The most notorious are the Chilean Salar de Atacama, and Uyuni in the Bolivian Altiplano. Despite the relevance of the region concerning the lithium resources, there is still scarce scientific literature on the hydrochemistry of lithium deposits in the Argentine portion of the Andean Plateau. In this article we present new hydrochemical data from the first regional-scale reconnaissance exploration of the four major salars in the northernmost Argentine Andes. Data revealed that brines in the studied salars are characterized by mean Li<sup>+</sup> concentrations ranging between 82 and 1,014 mg L<sup>-1</sup>, and mean Li:Mg ratios from 0.92 to 0.54. The size of the study salars becomes a potential limitation for the whole Li resources in comparison with the giant Atacama and Uyuni. Nonetheless, when considering the Li grade and the Li:Mg ratio of brines, the Northern Puna salars turn out to be very remarkable lithium prospects. Data emerged from this survey represent a valuable tool for: 1) private investment projects by defining Li mining targets, 2) for the administration of natural resources and the definition of the State's politics, and 3) for scientific purposes, especially in investigations meant to better understand the processes involved in the formation of Li brine deposits, salars, and endorheic basins.

**Keywords:** lithium, salars, Central Andes, Altiplano-Puna Plateau, hydrochemistry

## Introduction

Salars of the Central Andes are the largest lithium deposits on Earth (Warren 2010; Houston et al. 2011; Kesler et al. 2012; Munk et al. 2016). Particularly, the largest global resources concentrate in numerous internally drained basins of Chile, Bolivia and Argentina, where the lithium (Li) extraction has already become an important source of income in these South American countries. The Andean salars of Uyuni in Bolivia and Atacama in Chile (Fig. 1) contain the most important known Li resources in the world (Moraga et al. 1974; Gruber and Medina 2010; Mohr et al. 2010; Kunasz 2006; Kesler et al. 2012; Munk et al. 2016).

Uyuni is a spectacularly giant salar and with a surface of more than 10,500 km<sup>2</sup> it is the largest salt pan of the Andes and on Earth (Risacher and Fritz 1991; Kesler et al. 2012). This salt pan is located in the Altiplano at 3,663 m a.s.l. (Fig. 1). The mean Li content in the near-surface brines of Uyuni ranges from 316 to 602 mg L<sup>-1</sup> and the Li concentration pattern across the salar increases towards the south (Ericksen et al. 1976; Ericksen et al. 1977; Rettig et al. 1980; Risacher and Fritz 1991; Schmidt 2010). The estimated Li resources of Uyuni are over 10.2 Mt, which represent ~12 times the estimated resources of Greenbushes in Australia, the world famous Li pegmatite deposit (Kesler et al. 2012).

Although Uyuni is probably the most important Li resources worldwide, this salar is not in production yet. Much of the Li being produced globally at present is obtained from the Salar de Atacama. With estimated resources reaching 6.3 Mt, Atacama is thus the most important Li mine in the world (Moraga et al. 1974; Ide and Kunasz 1989; Kunasz 2006; Lowenstein and Risacher 2009; Gruber and Medina 2010; Mohr et al. 2010; Kesler et al. 2012; COCHILCO 2013).

The Salar de Atacama (Fig. 1) is a 3,000 km<sup>2</sup> salt pan located at 2,300 m a.s.l., whose halite nucleus spreads 1,100 km<sup>2</sup> and ~1,000 m depth (Moraga et al. 1974; Stoertz and Ericksen 1974; Bevacqua 1992; Alonso and Risacher 1996; Carmona et al. 2000; Boschetti et al. 2007; Jordan et al. 2007; Boutt et al. 2016; Corenthal et al. 2016). The average Li concentration of Atacama is ~1,400 mg L<sup>-1</sup>, ranging between 1,000 and 6,400 mg L<sup>-1</sup> (Moraga et al. 1974; Ide and Kunasz 1989; Kunasz 2006), representing the maximum Li concentration in a brine-type deposit reported to date worldwide. The Li concentration pattern across the Salar de Atacama is well known: five concentric Li grade zones were defined, with the higher Li grade zone located in the southern part of the salar (Ide and Kunasz 1989).

In the Argentine Puna region, in the southernmost part of the Andean Plateau (Fig. 1), there are also some remarkable Li prospects. The most prominent is the Salar de Hombre Muerto (Fig. 1), which became the

first Li mine operating in Argentina since the 90's (Kesler et al. 2012; Fornillo et al. 2015). Hombre Muerto comprises a 300 km<sup>2</sup> salt pan placed at 3,970 m a.s.l., with estimated Li resources of 0.8 Mt, and mean Li contents of ~520 mg L<sup>-1</sup>; the concentration pattern across the salar increases towards the south (Garrett 2004; Kesler et al. 2012; Godfrey et al. 2013).

As mentioned, the Li resources of salars in the Chilean Desierto de Atacama and the Bolivian Altiplano are largely known (Ericksen et al. 1977; Ide and Kunasz 1989; Risacher and Fritz 1991; Alonso and Risacher 1996; Risacher et al. 1999; Carmona et al. 2000; Risacher et al. 2003; Kunasz 2006; Risacher and Fritz 2009). On the contrary, and despite the relevance of this strategic mineral resource and the outstanding prospect of the Andean salars, there are still scarce scientific works on the hydrochemistry of Li deposits in the Argentinean Puna (Fig. 1). This region is becoming an increasing focus of exploration activity. Most of the available information of Puna salars is based on reports provided by mining companies and regional data reported in a number of scientific papers (Yaksic and Tilton 2009; Gruber and Medina 2010; King 2010; Houston et al. 2011; Fornillo et al. 2015; Munk et al. 2016). On the contrary, local works aiming to characterize the hydrochemistry of Li deposits in this Andean region are restricted to the Salar de Hombre Muerto (Godfrey et al. 2013; Fig. 1) and the Salar de Centenario-Ratones (Orberger et al. 2015) in the Southern Puna (Alonso et al. 1984), and the Guayatayoc playa lake in the Northern Puna (López Steinmetz 2017; Fig. 2). There are still many other salars in the Puna region that are promising Li prospects, and that – to date – were not object of scientific surveys, even of a reconnaissance nature. For instance, in the Northern Puna little is known about the hydrochemistry of the Cauchari and the Salinas Grandes salt pans, whereas the Salar de Jama remains completely unexplored (Fig. 2).

In this work we report the results of a regional Li exploration campaign covering an area of 9,000 km<sup>2</sup> in the endorheic Northern Puna (Fig. 2) that includes the four major salars which represent promising Li prospects. The major chemical composition and Li content of brine samples collected from the Salar de Jama, Olaroz, Cauchari and Salinas Grandes are analysed in order to contribute to the knowledge of the Andean salars hydrochemistry from a regional perspective. This research is the first scientific report on Li resources in the Northern Puna Plateau, and, along with the information previously reported by López Steinmetz (2017), completes the first broad survey of Li-bearing salars on the northern Argentine Plateau. We finally propose to discuss the Li resource perspectives of the Northern Puna region in the context of the most notorious Andean prospects.

## The study area

The salars analysed in this study are all set in the endorheic Northern Puna region (Fig. 2). The Salar de Jama is the smallest one, and is located on the Argentina-Chile border, at the foothills of the Jama volcano. Eastward, the Salar de Olaroz and Cauchari occupy the same north-south elongate orographic depression, superficially detached one from the other by prograding alluvial fans (the composite Archibarca alluvial cone). Finally, the Salinas Grandes covers the easternmost reaches of the lower Northern Puna, limiting to the north with the Guayatayoc salar basin.

There is an altitudinal gradient across the Northern Puna, which determines that western salars are placed at higher altitude than those located to east (Fig. 2). These four salars extend between 23° - 24°S. Northward, the endorheic basins of the Northern Puna are characterized by the presence of lakes that only occasionally dry out (e.g., Laguna de Pozuelos, McGlue et al. 2012; Laguna de Pululos, Lupo et al. 2006).

Orographic depressions that host salars are defined by north-south trending ranges formed during Andean thrusting events. These ranges expose the basement, which consist of Lower to Middle Ordovician (Santa Victoria Group, Turner 1960 a, b) and Precambrian - Eocambrian (Puncoviscana Formation, Turner 1960 a, b) metasedimentary rocks in the Puna Plateau and the Eastern Cordillera, respectively. The latter unit, together with Upper Cambrian sedimentary rocks (Meson Group, Turner 1960 a, b) are only present along the eastern border of the study area (Fig. 2). Middle to Upper Ordovician peraluminous, plutonic complexes and Jurassic to Cretaceous alkaline granites (Méndez et al. 1973; Zappettini 1989; Coira et al. 1999; Cristiani et al. 1999; Kirschbaum et al. 2006) are widely distributed in ranges along the western side of the Salinas Grandes and, in a lesser extent, along the eastern margin of the Salar de Olaroz (Fig. 2).

Cretaceous to Paleocene rift-related sedimentary rocks (Salta Group, Turner 1959) frequently crop out overlain by Upper Eocene to Upper Miocene synorogenic deposits (Turner 1972; Schwab 1973; Schwab and Lippolt 1974; Arias and Viera 1982; Seggiaro 2013). These units are widespread in the southern portions of the Tanque and Pircas ranges, and in the Alta range, in the southern border of the Salinas Grandes.

Paleogene to Lower Miocene continental red beds (Log Log, Vizcachera and Peña Colorada formations; see Coira et al. 2004; Seggiaro 2013; and references therein) were deposited afterwards in a broken foreland environment (e.g., del Papa et al. 2013), Fluvial to lacustrine deposits intercalated with air fall tuffs and pyroclastic flow deposits (Tiomayo, Trincheras and Pastos Chicos formations) characterise the Middle to Upper Miocene (16 to 10 Ma) sedimentary/volcanic record (Schwab and Lippolt 1974; Coira et al. 2004). Towards the Upper Miocene-Pliocene transition similar sedimentary sequences (Loma Blanca/Sijes Formation; Alonso 1986) locally involved deposition of evaporite facies (Olaroz-Coranzulí).

Large areas of the Northern Puna are covered by Upper Miocene-Pliocene and Pleistocene ignimbrites, dacite to rhyolite lavas and subvolcanic intrusions, and mafic andesite volcanic centres (Coira et al. 1993; Seggiaro 1994; Coira et al. 2004; Seggiaro 2013; Maro and Caffè 2016; and references therein). Quaternary alluvial fan deposits extend between the foot of the mountains and the flat areas, which are covered by fine-grained sediments and salt pans. Salar mining in the Northern Puna was traditionally related to the extraction of halite and ulexite from these salt pans, while Li mining started recently (2014), the Salar de Olaroz and Cauchari being the only active brine prospects (Fornillo et al. 2015).

The environmental conditions that prevail in these high-altitude endorheic basins are typically extreme, with low effective precipitation and wide temperature fluctuations. Thus, rainfall is markedly seasonal, with ~70% of the yearly total falling during the austral summer (December-March), while the dry season spans over the rest of the year. High rates of evaporation and low annual rainfall, averaging 150 - 400 mm and increasing from SW to NE, are responsible for a negative water balance. As a consequence, fluvial systems mainly consist of ephemeral streams. Despite most tributaries infiltrate before reaching the salars, some major fluvial collectors feed the systems over the year (Fig. 2). In addition, groundwater discharge probably represents an important source of water to the salar systems (Peralta Arnold et al. 2017).

## Methods

For the Li reconnaissance exploration and hydrochemical assessment of the Northern Puna salars, residual brines were sampled across the Salar de Jama (JA), Olaroz (OL), Cauchari (CA) and Salinas Grandes (SG, Fig. 3). The detailed location of samples is presented in Table A of the electronic supplementary material. Brine samples were collected and analysed during the austral spring 2010 (from September until December). Samples were collected at 40 to 90 cm depth in pits dug in salars, except for samples JA10, OL10, CA1, CA2 and SG10 that were collected from brine pools. Samples were stored in pre-cleaned polyethylene bottles and preserved refrigerated during transport.

Brine samples were analysed at the Agua de los Andes S. A. laboratory. Analytical results are summarized in Table 1. Physicochemical parameters such as pH and electrical conductivity were determined with a Hanna HI2314 multi-range conductivity meter. The major ion composition was determined following standard recommendations (Clesceri et al. 1998). Calcium ( $\text{Ca}^{2+}$ ) was determined by titration using a 0.01 M EDTA solution, while magnesium ( $\text{Mg}^{2+}$ ) was calculated as the difference between total hardness and calcium concentration. Chloride ( $\text{Cl}^-$ ) was determined by titration using the argentometric method. Sulphate ( $\text{SO}_4^{2-}$ ) was

precipitated in an acetic acid medium with  $\text{BaCl}_2$  and its concentration was determined by turbidimetry. Bicarbonate and carbonate ( $\text{HCO}_3^-$  and  $\text{CO}_3^{2-}$ ) were determined by titration using a 0.01 N sulfuric acid solution and methyl-orange and phenolphthalein were used as end-point indicators, respectively. Boron (B) was determined by colorimetry using carmine reactive. Sodium ( $\text{Na}^+$ ), potassium ( $\text{K}^+$ ) and lithium ( $\text{Li}^+$ ) were determined by Atomic Emission Spectroscopy. Ion balances were typically lower than 5% in all cases. Saturation index (SI) was calculated by using the PHREEQC 3.3.8 public domain and simulation program of the USGS, and employing the Pitzer database.

## Li-bearing salars of the Northern Puna

### *The Salar de Jama*

Jama is a north-south elongated salt pan located at 4,080 m a.s.l. The salar surface is 25 km<sup>2</sup>, spreading between 67°02' - 67°04'W and 23°15' - 23°21'S (Fig. 3A). Main tributaries are the Coruro, Lina and Pircas Rivers. Local lithology involves the Ordovician metasedimentary basement and Miocene - Pliocene ignimbrites (the Mucar, Atana and Toconao ignimbrites), dacite lavas as well as small mafic andesite volcanic centres (the Jama and Archibarca volcanoes). The salar overlies Quaternary alluvial deposits that interdigitate with a muddy salt shoreline along the south-eastern border of the salar.

Jama's brines are alkaline, with pH values ranging between 8.2 and 8.8 (Table 1), and moderately saline, with electrical conductivity values ranging between 12.33 and 183.63 mS cm<sup>-1</sup> (Table 1). According to their major chemical composition, brines are of the Na/Cl<sup>-</sup> - SO<sub>4</sub><sup>2-</sup> type, with relatively abundant Ca<sup>2+</sup> and K<sup>+</sup> (Fig. 4).

When the mean ionic concentration of Jama's brines is compared with those of the other Northern Puna salars, the Jama brines result the most dilute (Fig. 5). The Na:Cl ratios in the Jama brines are ~1 (Fig. 6A). The SO<sub>4</sub><sup>2-</sup> and Ca<sup>2+</sup> concentration pattern characterizes by a SO<sub>4</sub><sup>2-</sup>>Ca<sup>2+</sup> linear trend (Fig. 6B), except for the samples JA6, JA9 and JA10 that depict much higher SO<sub>4</sub><sup>2-</sup> concentrations.

Ratios near to 1 evidence salt recycling process, including halite and anhydrite/gypsum solubilisation and precipitation. According to saturation indexes (SI), these brines are unsaturated in anhydrite (SI from -2.19 to -1.41), gypsum (SI from -1.97 to -1.11), sylvite (SI from -4.29 to -2.11) and halite (SI from -3.60 to -1.43). According to this, the excess of SO<sub>4</sub><sup>2-</sup> over Ca<sup>2+</sup> (Fig. 6B) evidences the contribution of sulphate originated from the solubilisation of non-Ca sulphates and/or the scavenging of Ca<sup>2+</sup> by cation exchange and/or by

dolomite/calcite precipitation. Because brines are supersaturated with dolomite (IS from 0.33 to 1.07) and calcite (IS from 0.05 to 0.60) it seems that the latter should be the dominant process controlling  $\text{Ca}^{2+}$  concentrations in Jama's brines.

The  $\text{Li}^+$  concentration in the Jama's brines ranges between 1.5 and 262  $\text{mg L}^{-1}$ , with the highest Li grade zone along the north-western border of the salar (Fig. 7A). The mean  $\text{Li}^+$  concentration in the shallowest brines of the salar is 82  $\text{mg L}^{-1}$  while the mean Li:Mg ratio is 0.63 (Table 2). Borate concentrations in these brines range between 236 and 3,069  $\text{mg L}^{-1}$ ; no linear correlation between Li and B has been observed, being  $\text{Li} < \text{B}$  with the Li/B ratio up to 0.29 (Table 1).

### *The Salar de Olaroz and Cauchari*

These two salars are located in a N-S elongated basin at an average altitude of 3,903 m a.s.l. The Salar de Olaroz is a 130  $\text{km}^2$  salt pan spanning between  $66^\circ 39' - 66^\circ 45' \text{W}$  and  $23^\circ 24' - 23^\circ 33' \text{S}$  (Fig. 3B). The northern catchment area includes numerous hydrothermal springs, where the main fluvial collector is the Rosario River that discharges into the north of the salar. The other main tributary to the salar is the Archibarca River that reaches the salt pan from the west. This river forms a huge prograding alluvial fan that dissects the Olaroz - Cauchari topographic depression and acts as a barrier between the Olaroz (to the north) and the Cauchari salt pans.

The Salar the Cauchari is located at the southern part of the basin, between  $23^\circ 39' - 23^\circ 50' \text{S}$ , covering an area of  $\sim 80 \text{ km}^2$  (Fig. 3B). The dominant lithologies in the basin are sedimentary sequences and volcanic rocks. The Tocomar River is the major fluvial collector and reaches the salar from the south (Fig. 2). The southern catchment area includes numerous hydrothermal springs.

Shallow brines in both salars are circumneutral to alkaline, with pH values ranging between 8.1 and 8.5 in Olaroz and from 7.2 to 9.3 in Cauchari (Table 1). The brines' major chemical composition is dominated by  $\text{Na/Cl}^-$  type waters (Fig. 4), with electrical conductivity values and ionic contents that are up to one order of magnitude higher than those measured in the Jama's brines (from 184.85 to 320.15  $\text{mS cm}^{-1}$ , Fig. 5B). These values represent the highest ionic concentrations measured in the Northern Puna salars.

The  $\text{Na:Cl}$  ratios are  $\sim 1$  in Cauchari and  $\leq 1$  in Olaroz (Figure 6A). Despite this, brines are undersaturated with halite in both the Cauchari and the Olaroz salars (SI ranging from -1.44 to -0.91). Like Jama, the concentration of  $\text{SO}_4^{2-}$  is higher than  $\text{Ca}^{2+}$  in the Olaroz and Cauchari brines (Fig. 6B). This pattern could be the result of coupled reactions involving dissolution of gypsum/anhydrite and subsequent scavenging of  $\text{Ca}^{2+}$  by



dolomite/aragonite/calcite precipitation. In agreement, saturation indexes for anhydrite and gypsum vary from -3.29 to -2.11 and -3.16 to -1.92, respectively. However, brines are supersaturated with carbonates only in the northern Cauchari area (the  $SI_{\text{dolomite}}$  ranges from 0.44 to 1.40 in samples CA1, CA2 and CA3, the  $SI_{\text{aragonite}}$  is 0.24 in the CA2, and the  $SI_{\text{calcite}}$  varies from 0.08 to 0.38 in samples CA2 and CA3), but are undersaturated in the southern Cauchari and the entire Olaroz ( $SI_{\text{dolomite}}$ : -1.56 to -0.16;  $SI_{\text{aragonite}}$ : -1.37 to -0.07;  $SI_{\text{calcite}}$ : -1.22 to -0.22). These values evidence thermodynamically optimum conditions for locally constrained carbonate precipitation and sulphate dissolution, leading to the concomitant existence of sulphated-rich inputs.

The  $Li^+$  concentration in shallow brines ranges from 771 – 1,213 mg L<sup>-1</sup> in Olaroz and 442 – 1,739 mg L<sup>-1</sup> in Cauchari. The highest Li grade zones occupy the central area of these two salars (Fig. 7B and C). The mean  $Li^+$  concentration is 860 mg L<sup>-1</sup> in Cauchari and 1,014 mg L<sup>-1</sup> in Olaroz, the Li:Mg ratios are 0.86 and 0.89, respectively (Table 2). The borate concentration in these brines varies between 1,336 and 3,175 mg L<sup>-1</sup> (Table 1) and do not show a linear correlation with Li contents, with  $Li < B$  and the Li/B ratio up to 0.96 in Cauchari and 0.29 in Olaroz.

### *The Salinas Grandes*

Salinas Grandes is a large salt pan of 280 km<sup>2</sup> placed at 3,410 m a.s.l. between 23°33' - 23°45'S and 65°51' - 66°12'W (Fig. 3C). This salar developed south of the Las Burras alluvial fan, which separates the Salinas Grandes salt pan from the Guayatayoc playa lake to the north. Permanent streams feeding the Salinas Grandes include the San Antonio de los Cobres and the El Moreno Rivers. The southern catchment area of the San Antonio de los Cobres River includes numerous hydrothermal springs, while the headwater area of the El Moreno basin involves seasonal periglacial processes. Muddy salt shorelines associated to the mouth of the El Moreno River are mainly developed along the south-eastern border of the salt pan. Quaternary alluvial deposits cover the low lying areas and reach the foot of mountains. The metasedimentary basement and the Cretaceous to Paleocene sedimentary sequences are the most widespread lithologies along the eastern side of the basin, while Paleozoic and Mesozoic plutonic rocks outcrop in the west-boundary ranges.

Similar to other salars of the study area, shallow brines in the Salinas Grandes are circumneutral to slightly alkaline, with pH ranging from 7.1 and 8.0 (Table 1). Electrical conductivity show intermediate values compared with the remaining salars of the Northern Puna, typically ranging between 232.18 and 241.08 mS cm<sup>-1</sup> (Fig. 5B). Major ionic concentrations are dominated by Na and Cl ions (Fig. 4). Interestingly, these brines show the largest variability of the ionic concentrations compared with the neighbour salars (Fig. 5). The sample SG1 is

the most diluted (conductivity = 233.85 mS cm<sup>-1</sup>) and characterizes by the lowest Ca<sup>2+</sup> concentration compared with the remaining samples collected from the Salinas Grandes (Fig. 5), and a Na:Cl ratio ~1 (Fig. 6A). Conversely, the sample SG7 contains high Mg<sup>2+</sup> and K<sup>+</sup> concentrations, even when compared with the other salars of the Northern Puna (Fig. 5A). The Salinas Grandes brines also show nearly equivalent proportions of Ca<sup>2+</sup>, Mg<sup>2+</sup> and K<sup>+</sup> with Ca:Mg ~1 (Fig. 4), and typically have Ca<sup>2+</sup> > SO<sub>4</sub><sup>2-</sup> (Fig. 6B). Saturation indexes indicate that brines are undersaturated in calcite, aragonite, and dolomite (SI<sub>dolomite</sub>: -2.07 and -1.55, SI<sub>aragonite</sub>: -1.30 to -1.11 and the SI<sub>calcite</sub>: -1.15 and -0.97).

The equivalent concentrations of Li and borate through the salar are similar (Fig. 5A), with the Li:B ratio close to 1 in samples SG4, SG6 and SG9 (Li/B of 0.95, 1.10 and 0.99, respectively), Li>B in samples 5, 8 and 10 (from 1.17 to 1.32), and Li<B in the remaining samples (SG1 = 0.07, SG2 = 0.67 and SG3 = 0.70). The concentration of borate is from 309 and up to 542 mg L<sup>-1</sup>, and Li<sup>+</sup> ranges between 25 and 1,018 mg L<sup>-1</sup>, with the highest Li grade zone located at the western margin of the salar (Fig. 7D). The mean Li<sup>+</sup> concentration is 332 mg L<sup>-1</sup> and the mean Li:Mg ratio is 0.54 (Table2).

## DISCUSSION

The major chemical composition of the studied brines is rather constant; most samples are of the Na/Cl type with some subordinated samples of the Na/Cl-SO<sub>4</sub><sup>2-</sup> type. Thus, the highly concentrated brines are typically rich in Na<sup>+</sup> and Cl<sup>-</sup>, and relatively poor in Ca<sup>2+</sup>, Mg<sup>2+</sup> and HCO<sub>3</sub><sup>-</sup> + CO<sub>3</sub><sup>2-</sup>. An additional common feature in the Northern Puna brines is that K<sup>+</sup> concentrations are from 2 to 6 times higher than those of Mg<sup>2+</sup>. However, the most conspicuous feature is the high Li grades, with average concentrations from 82 to 1,014 mg L<sup>-1</sup>, the highest ones found in the Cauchari and Olaroz salt pans.

Hydrochemical features of the Andean salars are controlled by a number of variables acting at different scales. In a recent work, Munk et al. (2016) have defined six major features shared by most Li-rich brines deposits at a global scale: (1) arid climate; (2) closed basin containing a salar (salt crust), a salt lake, or both; (3) associated igneous and/or hydrothermal activity; (4) tectonically driven subsidence; (5) suitable Li sources; and (6) sufficient time to concentrate Li in the brine. However, even though all these features converge across the Puna Plateau, brines from the studied salars have an uneven distribution of Li grades. Therefore, there must be some local factors constraining the higher concentrations of Li to some particular systems.

Some *in situ* processes that are taking place within the salars are conditioned by the ionic content and salinity (Fig. 5) of the study brines. In the four studied salars, average salinity is the highest in Olaroz and the

lowest in Jama, while intermediate values were measured in Cauchari and Salinas Grandes. In addition to salinity, the concentration pattern  $OL \geq CA \geq SG \geq JA$  is valid for  $Mg^{2+}$ ,  $K^+$ ,  $Li^+$  and  $BO_3^{3-}$  concentrations, but not for  $Ca^{2+}$ , whose regional concentration pattern is  $SG \geq JA \geq CA \geq OL$ . The lower  $Ca^{2+}$  concentrations observed in Olaroz and Cauchari are the consequence of local geochemical processes that involve precipitation of calcite/aragonite but also of some other Ca-scavenging process such as cation exchange. The latter mechanism might occur during the interaction between Ca-rich solutions and clay minerals accumulated in the salt pan.

Residual brines in Northern Puna salars are characterized by a final major composition dominated by  $Na^+$  -  $Cl^-$  and  $SO_4^{2-}$  ions, which is one typical end member in the chemical divide trend proposed by Hardie and Eugster (1970). The behaviour of trace elements such as Li and borate in the context of this chemical divide has been scarcely assessed. For example, Witherow and Lyons (2011) determined on the basis of geochemical modelling that Li is largely conservative in water samples of the Great Basin (USA), Saskatchewan, and the McMurdo Dry Valleys of Antarctica and, thus, its concentration is the result of long-term solute input and concentration through evaporation and/or sublimation processes. According to this, Li behaves as an incompatible element, not only during the stages of magmatic differentiation but also during weathering (Munk et al. 2016). Therefore, its concentration during brine evolution should follow an increasing trend with increasing water salinity. However, we have observed no unequivocal correlation between the Li grade of brines and conductivity nor other conservative solutes such as Na and Cl. For instance, as shown in Figure 8A, the Jama and Cauchari samples have a remarkable Li/Conductivity correlation, but brines from the Salinas Grandes and Olaroz show Li concentrations that increase independently from salinity (Fig. 8A). This suggests that during the sediment-water interaction, Li ions may in some extent co-precipitate as an impurity in the minerals present in the saline crusts and efflorescens or it could be adsorbed onto clay minerals due to the capacity of  $Li^+$  to be incorporated into the smectite interlayers (e.g., Zhang et al. 1998; William and Herving 2002).

The hydrothermal activity is considered as one of the most significant factors for the formation of Li and boron rich brines in the Central Andes (Risacher et al. 2003; Godfrey et al. 2013; López Steinmetz 2017; and references therein). Indeed, a number of authors indicated that the main sources of Li in Uyuni and the nearby salars of Coipasa and Empexa in the southern part of the Bolivian Altiplano are thermal springs associated with Quaternary rhyolitic volcanism (Shcherbakov and Dvorov 1970; Ericksen et al. 1977; Campbell 2009). Since hydrothermal activity on the region is largely related to volcanism and the formation of the plateau (i.e., Isacks 1988; de Silva 1989; Allmendinger et al. 1997; McQuarrie et al. 2002; Kay et al. 2010; Perkins et al. 2016; and

references therein), it could be considered that this regionally pervasive and large scale process is most likely a primary condition for the formation of exceptional Li brine-type deposits on the Argentine Puna region.

The data that we present in this contribution clearly reveal that in the Norther Puna region, the highest concentrations of Li are restricted to the Olaroz and Cauchari salt pans (Fig. 7). These two salars are located in the same tectonically N-S elongated depression. Therefore, the distinctive Li enrichment in Olaroz and Cauchari is being locally influenced by basin-scale processes, such as the characteristics and density (in terms of the quantity of springs that exist in the basin) of geothermal fields, the weathering of Li-rich lithologies, and/or geochemical processes taking place within the salars. An additional local driving factor on increasing the Li grade in the Olaroz and Cauchari's brines should likely be associated to the role of major thrusts on transporting fluids from the deepest zones of the upper crust and generating large ionic remobilizations. For example, Franco et al. (2016) reported the presence of thermal springs discharging at the location of the basin bounding structures along the marginal zones of the Salar de Olaroz. Additionally, the basin involves several hydrothermal fields directly associated with volcanic centers (Peralta Arnold et al. 2016). Therefore, hydrothermal springs in the Salar de Olaroz and Cauchari are likely related to the presence of volcanic centers, which include isolated edifices along oblique volcanic belts (e.g., Presta and Caffè 2014; Maro et al. 2016) and large volcanic complex calderas (Seggiaro 1994; Seggiaro 2013).

The lower Li grade in brines from the Salinas Grandes relative to Olaroz and Cauchari could be associated with several characteristics of the basin: 1) the catchment lithology is dominated by the Eastern Cordillera basement, which is different from that of the Northern Puna, and would, therefore, have a different geochemical signature; 2) the lack of large hydrothermal fields and volcanic rock outcrops; and 3) the less arid conditions in the basin's catchments located at the easternmost edge of the Norther Puna region. Consequently, even if the hydrothermal activity - which represents just one of the multiple expressions related to the intrinsic nature of the plateau - is considered as a major source for Li supply, additional geological, climatic, and geochemical aspects locally generating distinctive Li grades and brine compositions in every salt pan and/or basin should also be considered.

In order to compare the relative abundance of ionic species in different salars, or between samples from the same salar with uneven salinities, it is necessary to remove the effect of the evaporative concentration. The relative abundance of  $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$ ,  $\text{K}^{+}$ ,  $\text{Li}^{+}$  and  $\text{BO}_3^{3-}$  in salars from the Northern Puna is presented in Figure 9. In this diagram, the evaporative effect was removed by employing TDS (total dissolved solids, for TDS method see caption of Fig. 9) normalized values. This diagram is substantially different from Figure 5 where plotted data

involve absolute ionic concentrations (the amount of ionic species that could be obtained from one litre of brine). Normalized concentrations revealed that the four salars contain similar proportions of  $\text{Ca}^{2+}$ , the Salinas Grandes brines are proportionally richer in  $\text{K}^{+}$  and  $\text{BO}_3^{3-}$ , and the Salar de Cauchari contains proportionally higher  $\text{Li}^{+}$  concentrations than its neighbour Northern Puna salars (Fig.8). This suggests that if a brine sample from the salar de Jama (which is less saline than brines from Cauchari) is hypothetically evaporated in order to increase its salinity up to the values of Cauchari, then, one litre of the Jama brine would still have a lower Li grade than the same volume of the Cauchari brine. Consequently, the evaporative concentration process of such brines would be more efficient for Li recovering at Cauchari than Jama. This statement seems an evident matter when comparing Cauchari and Jama's brines because the mean  $\text{Li}^{+}$  concentration of Cauchari is  $860 \text{ mg L}^{-1}$  and that of Jama is  $82 \text{ mg L}^{-1}$  (Table 2). However, the extrapolation of this rule to the other salars of the Northern Puna (Fig. 9) allows stating that the evaporative concentration process in Cauchari is more efficient than in Olaroz (even if the mean  $\text{Li}^{+}$  concentration of the latter reaches  $1,014 \text{ mg L}^{-1}$  versus  $860 \text{ mg L}^{-1}$  of the former).

The integrated analysis of the Li-rich brine chemistry from Northern Puna provides important information to evaluate the potentially economic viability of these brines with respect to Li extraction. In addition to the Li grade of brines, the substrate porosity-permeability, the aquifer water balance, and the volume of the host aquifer (Houston et al. 2011), the magnesium content is an additional issue regarding the Li-mining process because  $\text{Mg}^{2+}$  causes chemical interferences in the brine purification process and limits the  $\text{Li}^{+}$  recovering (e.g., Crespo et al. 1987; An et al. 2012; Kesler et al. 2012; An et al. 2012). The Uyuni's brines typically have high grade  $\text{Mg}^{2+}$  (Ericksen et al. 1978; Risacher and Fritz 1991) while the Salar de Hombre Muerto represents the opposite situation, with low magnesium contents (Kesler et al. 2012; Godfrey et al. 2013; Table 2, Fig. 8B). The Li:Mg ratios in the Northern Puna range from 0.54 to 0.92 (Table 2), which in the regional context make them closer to Hombre Muerto than to Uyuni (Fig. 8B).

Economically viable Li-rich brines in the Central Andes contain varying amounts of the major cations and anions ( $\text{Na}^{+}$ ,  $\text{K}^{+}$ ,  $\text{Mg}^{2+}$ ,  $\text{Ca}^{2+}$ ,  $\text{Cl}^{-}$ ,  $\text{SO}_4^{2-}$ , and  $\text{CO}_3^{2-}$ ), which can form a wide range of ionic brine compositions. In general, the Northern Puna's brines contain less  $\text{Mg}^{2+}$  than those accumulated in Atacama and Uyuni (Fig. 8B). Nonetheless, the extremely high  $\text{Li}^{+}$  concentration of Atacama remains the most important difference between all these salars (Table 2). An additional and substantial difference is the oversized surface of Uyuni and Atacama compared with the dimension of the Northern Puna salars. These two aspects, the  $\text{Li}^{+}$  concentration and the salar size, are potentially limiting the whole resources of the Northern Puna salt pans.

However, when considering the Li grade and the Li:Mg ratio of brines, the Northern Puna salt pans are revealed as very remarkable Li prospects.

## Conclusion

This study reports the results of a regional Li exploration campaign covering an area of 9,000 km<sup>2</sup> in the Northern Puna that included the four major salars in the region. These evaporite systems represent remarkable Li prospects with mean Li<sup>+</sup> concentrations varying between 82 and 1,014 mg L<sup>-1</sup>, and mean Li:Mg ratios ranging from 0.92 to 0.54.

The major chemical composition of the studied brines is rather constant; most samples are of the Na/Cl type with some subordinated samples with a major ionic composition of the Na/Cl-SO<sub>4</sub><sup>2-</sup> type, and with K>Mg. Evaporative concentration, dissolution/precipitation of halite and gypsum/anhydrite, and the precipitation of calcite/aragonite/dolomite are important processes controlling the major chemical composition of brines. Unlike major ions, the concentrations of minor elements such as Mg<sup>2+</sup>, Li<sup>+</sup> and BO<sub>3</sub><sup>3-</sup> do not show clear correlation with salinity, which suggest that some other factors are controlling their spatial distribution in the shallowest brines of the studied salars. The absence of a geographical/geomorphological pattern for the ionic concentrations suggests that the hydrochemistry of salars is being partially conditioned by local and regional intrinsic characteristics of each basin, as well as by regional features related to the geological/tectonic nature of the Andean Plateau. These characteristics are likely responsible for the higher Li concentrations in the N-S depression occupied by the Olaroz and Cauchari salars compared with the neighbour salars located towards the margins of the northern Puna region.

The relationship between the Li grade and brine salinity indicates that the evaporative Li recovering should be more efficient in Cauchari than in the remaining salars of the Northern Puna. Despite that the salar dimension is a factor potentially limiting the whole Li resources in the Northern Puna, especially when comparing with Atacama and Uyuni, the Li grade and the Li:Mg ratio in the Northern Puna brines are defining outstanding perspectives for the salt pans of this Andean region.

## ACKNOWLEDGMENTS

This study was founded by the PRH Red 101 ANPCyT of the Argentine National Government and the National University of Jujuy. R.L. López Steinmetz thanks the grant E/B003 of the SECTER - UNJu. Other funds came from projects PIO CONICET-UNJu 14020140100010CO, and FONARSEC-FITR Industria 2013 N°

391 9 (ANPCyT). The laboratory of Aguas de los Andes S. A. provided lab facilities and the Instituto de Geología y  
392 Minería (Universidad Nacional de Jujuy) complemented field logistics. The authors thank Ing. Maria Silvina  
393 Muhana Senn and Mr. Luis Omar Villegas from the Agua de los Andes laboratory for analytical advising, and  
394 also inhabitants from the communities of the Jujuy's Puna for their hospitality. Special thanks to Captain  
395 Christian Meuric for large field logistical support.

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# 581 **Figure captions**

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583 Fig.1. Map of the Andean Plateau (dark green area), showing the location of the Salar de Atacama, Uyuni and  
 584 Hombre Muerto (white areas). Thick dashed grey lines indicate the internal Plateau boundaries between the  
 585 Bolivian Altiplano, the Argentinean Northern and Southern Puna (Alonso et al. 1984). There are many other  
 586 salars in the Chilean Desierto de Atacama, in the Bolivian Altiplano and in the Argentinean Puna Plateau that are  
 587 not shown in this map.

588

589 Fig. 2. Simplified geologic map of the Northern Puna Plateau between 23°06'S and 23°56'S, modified from  
 590 González et al. (2000), Coira et al. (2004), and Seggiaro (2013). The map shows the location of the Northern  
 591 Puna's salars. A-A' is the altitudinal transect of the Northern Puna Plateau at 23°30'S. Lithological legend: 1)  
 592 modern salar; 2) Quaternary alluvial deposits, including piedmonts, alluvial fans and alluvial plains; 3)  
 593 sedimentary units including the Cretaceous-Paleocene rift related and the Upper Eocene to Upper Miocene  
 594 synorogenic deposits; 4) Plio-Pleistocene ignimbrite; 5) Miocene-Pliocene ignimbrite; 6) Miocene dacite; 7)  
 595 Jurassic-Cretaceous granite; 8) Ordovician granite; 9) Ordovician metasedimentary basement of the Northern

Puna; 10) Precambrian - Eocambrian metasedimentary basement of the Eastern Cordillera and Upper Cambrian sedimentary units.

Fig. 3. Maps showing the location of shallow brine sampling points in the Salar de Jama (A), Olaroz, Cauchari (B) and Salinas Grandes (C). Precise latitude and longitude of the samples are given in Table A of the electronic supplementary material.

Fig. 4. Ternary diagrams showing the relative ionic concentrations of brines from the Salar de Jama (JA), Olaroz (OL), Cauchari (CA) and Salinas Grandes (SG). Ionic concentrations are expressed in meq L<sup>-1</sup>.

Fig. 5. Comparative concentrations of Ca<sup>2+</sup>, Mg<sup>2+</sup>, K<sup>+</sup>, Li<sup>+</sup> and BO<sub>3</sub><sup>3-</sup> (A) and electrical conductivity (B) of samples collected from the Salar de Jama (JA), Olaroz (OL), Cauchari (CA) and Salinas Grandes (SG).

Fig. 6. Scatter diagrams showing the variation of Na<sup>+</sup> versus Cl<sup>-</sup> (A) and Ca<sup>2+</sup> versus SO<sub>4</sub><sup>2-</sup> (B and C) in the studied brines. Abbreviations are: Jama (JA), Olaroz (OL), Cauchari (CA), Salinas Grandes (SG), Guayatayoc (G), Hombre Muerto (HM), Uyuni (UYU) and Atacama (ATA). The HM data were taken from Godfrey et al. (2013). The UYU samples UB and UE and the ATA data set are from Risacher and Fritz (2009). The UYU samples 109, 128 and 120 were taken from Ericksen et al. (1977). The G samples are from Lopez Steinmetz (2017) and samples JA, OL, CA and SG are from this contribution. The HM samples 10, 11 and 12 are lagoon brines, sample 13 is a brine collected at 200 cm depth in a hole drilled into the salar (Godfrey et al. 2013). The UYU samples UB and UE correspond to brines collected at 100 cm depth (Risacher and Fritz 2009), sample 109 was collected in a brine pool and samples 120 and 128 are brines collected from holes drilled 40 to 50 cm into the salt crust (Ericksen et al. 1977). Samples GG<sub>3</sub>, GG<sub>4</sub> and GQ<sub>0</sub> were collected from pits dug in the playa lake sediments (Lopez Steinmetz 2017).

Fig. 7. Li grade zones in the four major salars of the Northern Puna Plateau. Brine Li concentrations are in mg L<sup>-1</sup>.

Fig. 8. Scatter diagrams showing the variation of (Na<sup>+</sup>+Cl<sup>-</sup>) and Conductivity with Li<sup>+</sup> (A) and Li<sup>+</sup> versus Mg<sup>2+</sup> (B and C) in the studied brines. Jama (JA), Olaroz (OL), Cauchari (CA), Salinas Grandes (SG). Data

corresponding to Guayatayoc (G), Hombre Muerto (HM), Uyuni (UYU) and Atacama (ATA) are plotted for comparison. Details concerning the HM, UYU, ATA and G plotted data are presented in caption of Fig. 6.

Fig. 9. Comparative  $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$ ,  $\text{K}^+$ ,  $\text{Li}^+$  and  $\text{BO}_3^{3-}$  concentration ranges of samples collected from the Salar de Jama (JA), Olaroz (OL), Cauchari (CA) and Salinas Grandes (SG). The TDS value was obtained from electrical conductivity, by employing a conversion factor of 1 ( $\text{TDS} = \text{Conductivity}$ ) based on the relation between the concentration of all the analysed ions relative to conductivity (Fig. A of the electronic supplementary material).

Table 1. Chemical composition of brines samples collected in the Salar de Jama (JA), Olaroz (OL), Cauchari (CA) and Salinas Grandes (SG).

Table 2. Comparative attributes of the Northern Puna's salars and Atacama, Uyuni and Hombre Muerto. The mean  $\text{Li}^+$  concentration and Li:Mg ratios of Jama, Olaroz, Cauchari and Salinas Grandes were settled based on original data from this contribution (Table 1). The mean  $\text{Li}^+$  concentration and Li:Mg of Guayatayoc correspond to the mean value of the 3 brine samples (samples G3, G4 and Q0) reported in Lopez Steinmetz (2017). The mean  $\text{Li}^+$  concentration reported for Atacama are from Ide and Kunasz (1989) and Kunasz (2006), and the mean Li:Mg corresponds to values reported by COCHILCO (2013). The mean  $\text{Li}^{+a}$  concentration and Li:Mg<sup>a</sup> ratio in Uyuni corresponds to the mean values of 38 samples (from sample 100 to sample 133 and samples 146, 147 and 147A) reported by Ericksen et al. (1977). The mean  $\text{Li}^{+b}$  concentration and Li:Mg<sup>b</sup> ratio corresponds to the mean values of the 164 samples (from sample UA to sample RZ) reported by Risacher and Fritz (1991). The mean  $\text{Li}^{+c}$  concentration and Li:Mg ratio of Hombre Muerto correspond to the mean value of the 9 samples (samples 4, 5, 6 and 9 to 14) reported by Godfrey et al. (2013). The mean  $\text{Li}^{+d}$  concentration in Hombre Muerto corresponds to the mean  $\text{Li}^+$  concentration of 100 cm-deep brines reported by Garrett (2004) and Kesler et al. (2012).