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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⁺ concentrations ranging between 82 and 1,014 mg L⁻¹, 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

33

34 **Introduction**

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

41 Uyuni is a spectacularly giant salar and with a surface of more than 10,500 km² it is the largest salt pan
42 of the Andes and on Earth (Risacher and Fritz 1991; Kesler et al. 2012). This salt pan is located in the Altiplano
43 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⁻¹
44 and the **Li** concentration pattern across the salar increases towards the south (Ericksen et al. 1976; Ericksen et al.
45 1977; Rettig et al. 1980; Risacher and Fritz 1991; Schmidt 2010). The estimated **Li** resources of Uyuni are over
46 10.2 Mt, which represent ~12 times the estimated resources of Greenbushes in Australia, the world famous **Li**
47 pegmatite deposit (Kesler et al. 2012).

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

53 The Salar de Atacama (Fig. 1) is a 3,000 km² salt pan located at 2,300 m a.s.l., whose halite nucleus
54 spreads 1,100 km² and ~1,000 m depth (Moraga et al. 1974; Stoertz and Ericksen 1974; Bevacqua 1992; Alonso
55 and Risacher 1996; Carmona et al. 2000; Boschetti et al. 2007; [Jordan et al. 2007](#); [Boutt et al. 2016](#); [Corenthal et al. 2016](#)).
56 The average **Li** concentration of Atacama is ~1,400 mg L⁻¹, ranging between 1,000 and 6,400 mg L⁻¹
57 (Moraga et al. 1974; Ide and Kunasz 1989; Kunasz 2006), representing the maximum **Li** concentration in a
58 brine-type deposit reported to date worldwide. The **Li** concentration pattern across the Salar de Atacama is well
59 known: five concentric **Li** grade zones were defined, with the higher **Li** grade zone located in the southern part of
60 the salar (Ide and Kunasz 1989).

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

63 first Li mine operating in Argentina since the 90's (Kesler et al. 2012; Fornillo et al. 2015). Hombre Muerto
64 comprises a 300 km² salt pan placed at 3,970 m a.s.l., with estimated Li resources of 0.8 Mt, and mean Li
65 contents of ~520 mg L⁻¹; the concentration pattern across the salar increases towards the south (Garrett 2004;
66 Kesler et al. 2012; Godfrey et al. 2013).

67 As mentioned, the Li resources of salars in the Chilean Desierto de Atacama and the Bolivian Altiplano
68 are largely known (Ericksen et al. 1977; Ide and Kunasz 1989; Risacher and Fritz 1991; Alonso and Risacher
69 1996; Risacher et al. 1999; Carmona et al. 2000; Risacher et al. 2003; Kunasz 2006; Risacher and Fritz 2009).
70 On the contrary, and despite the relevance of this strategic mineral resource and the outstanding prospect of the
71 Andean salars, there are still scarce scientific works on the hydrochemistry of Li deposits in the Argentinean
72 Puna (Fig. 1). This region is becoming an increasing focus of exploration activity. Most of the available
73 information of Puna salars is based on reports provided by mining companies and regional data reported in a
74 number of scientific papers (Yaksic and Tilton 2009; Gruber and Medina 2010; King 2010; Houston et al. 2011;
75 Fornillo et al. 2015; Munk et al. 2016). On the contrary, local works aiming to characterize the hydrochemistry
76 of Li deposits in this Andean region are restricted to the Salar de Hombre Muerto (Godfrey et al. 2013; Fig. 1)
77 and the Salar de Centenario-Ratones (Orberger et al. 2015) in the Southern Puna (Alonso et al. 1984), and the
78 Guayatayoc playa lake in the Northern Puna (López Steinmetz 2017; Fig. 2). There are still many other salars in
79 the Puna region that are promising Li prospects, and that – to date – were not object of scientific surveys, even of
80 a reconnaissance nature. For instance, in the Northern Puna little is known about the hydrochemistry of the
81 Cauchari and the Salinas Grandes salt pans, whereas the Salar de Jama remains completely unexplored (Fig. 2).

82 In this work we report the results of a regional Li exploration campaign covering an area of 9,000 km²
83 in the endorheic Northern Puna (Fig. 2) that includes the four major salars which represent promising Li
84 prospects. The major chemical composition and Li content of brine samples collected from the Salar de Jama,
85 Olaroz, Cauchari and Salinas Grandes are analysed in order to contribute to the knowledge of the Andean salars
86 hydrochemistry from a regional perspective. This research is the first scientific report on Li resources in the
87 Northern Puna Plateau, and, along with the information previously reported by López Steinmetz (2017),
88 completes the first broad survey of Li-bearing salars on the northern Argentine Plateau. We finally propose to
89 discuss the Li resource perspectives of the Northern Puna region in the context of the most notorious Andean
90 prospects.

91

92 **The study area**

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

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

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

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

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

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

130 The environmental conditions that prevail in these high-altitude endorheic basins are typically extreme,
131 with low effective precipitation and wide temperature fluctuations. Thus, rainfall is markedly seasonal, with
132 ~70% of the yearly total falling during the austral summer (December-March), while the dry season spans over
133 the rest of the year. High rates of evaporation and low annual rainfall, averaging 150 - 400 mm and increasing
134 from SW to NE, are responsible for a negative water balance. As a consequence, fluvial systems mainly consist
135 of ephemeral streams. Despite most tributaries infiltrate before reaching the salars, some major fluvial collectors
136 feed the systems over the year (Fig. 2). In addition, groundwater discharge probably represents an important
137 source of water to the salar systems (Peralta Arnold et al. 2017).

138

139 **Methods**

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

147 Brine samples were analysed at the Agua de los Andes S. A. laboratory. Analytical results are
148 summarized in Table 1. Physicochemical parameters such as pH and electrical conductivity were determined
149 with a Hanna HI2314 multi-range conductivity meter. The major ion composition was determined following
150 standard recommendations (Clesceri et al. 1998). Calcium (Ca^{2+}) was determined by titration using a 0.01 M
151 EDTA solution, while magnesium (Mg^{2+}) was calculated as the difference between total hardness and calcium
152 concentration. Chloride (Cl^-) was determined by titration using the argentometric method. Sulphate (SO_4^{2-}) was

153 precipitated in an acetic acid medium with BaCl₂ and its concentration was determined by turbidimetry.
154 Bicarbonate and carbonate (HCO₃⁻ and CO₃²⁻) were determined by titration using a 0.01 N sulfuric acid solution
155 and methyl-orange and phenolphthalein were used as end-point indicators, respectively. Boron (B) was
156 determined by colorimetry using carmine reactive. Sodium (Na⁺), potassium (K⁺) and lithium (Li⁺) were
157 determined by Atomic Emission Spectroscopy. Ion balances were typically lower than 5% in all cases.
158 Saturation index (SI) was calculated by using the PHREEQC 3.3.8 public domain and simulation program of the
159 USGS, and employing the Pitzer database.

160

161 **Li-bearing salars of the Northern Puna**

162

163 *The Salar de Jama*

164 Jama is a north-south elongated salt pan located at 4,080 m a.s.l. The salar surface is 25 km², spreading
165 between 67°02' - 67°04'W and 23°15' - 23°21'S (Fig. 3A). Main tributaries are the Coruro, Lina and Pircas
166 Rivers. Local lithology involves the Ordovician metasedimentary basement and Miocene - Pliocene ignimbrites
167 (the Mucar, Atana and Toconao ignimbrites), dacite lavas as well as small mafic andesite volcanic centres (the
168 Jama and Archibarca volcanoes). The salar overlies Quaternary alluvial deposits that interdigitate with a muddy
169 salt shoreline along the south-eastern border of the salar.

170 Jama's brines are alkaline, with pH values ranging between 8.2 and 8.8 (Table 1), and moderately
171 saline, with electrical conductivity values ranging between 12.33 and 183.63 mS cm⁻¹ (Table 1). According to
172 their major chemical composition, brines are of the Na/Cl⁻ - SO₄²⁻ type, with relatively abundant Ca²⁺ and K⁺
173 (Fig. 4).

174 When the mean ionic concentration of Jama's brines is compared with those of the other Northern Puna
175 salars, the Jama brines result the most dilute (Fig. 5). The Na:Cl ratios in the Jama brines are ~1 (Fig. 6A). The
176 SO₄²⁻ and Ca²⁺ concentration pattern characterizes by a SO₄²⁻>Ca²⁺ linear trend (Fig. 6B), **except** for the **samples**
177 **JA6, JA9 and JA10** that depict **much** higher SO₄²⁻ concentrations.

178 Ratios near to 1 evidence salt recycling process, including halite and anhydrite/gypsum solubilisation
179 and precipitation. According to saturation indexes (SI), these brines are unsaturated in anhydrite (SI from -2.19
180 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).
181 According to this, the excess of SO₄²⁻ over Ca²⁺ (Fig. 6B) evidences the contribution of sulphate originated from
182 the solubilisation of non-Ca sulphates and/or the scavenging of Ca²⁺ by **cation exchange and/or by**

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

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

191

192 *The Salar de Olaroz and Cauchari*

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

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

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

209 The Na:Cl ratios are ~ 1 in Cauchari and ≤ 1 in Olaroz (Figure 6A). Despite this, brines are
210 undersaturated with halite in both the Cauchari and the Olaroz salars (SI ranging from -1.44 to -0.91). Like Jama,
211 the concentration of SO_4^{2-} is higher than Ca^{2+} in the Olaroz and Cauchari brines (Fig. 6B). This pattern could be
212 the result of coupled reactions involving dissolution of gypsum/anhydrite and subsequent scavenging of Ca^{2+} by

213 dolomite/aragonite/calcite precipitation. In agreement, saturation indexes for anhydrite and gypsum vary from -
214 3.29 to -2.11 and -3.16 to -1.92, respectively. However, brines are supersaturated with carbonates only in the
215 northern Cauchari area (the SI_{dolomite} ranges from 0.44 to 1.40 in samples CA1, CA2 and CA3, the $SI_{\text{aragonite}}$ is
216 0.24 in the CA2, and the SI_{calcite} varies from 0.08 to 0.38 in samples CA2 and CA3), but are **undersaturated** in the
217 southern Cauchari and the entire Olaroz (SI_{dolomite} : -1.56 to -0.16; $SI_{\text{aragonite}}$: -1.37 to -0.07; SI_{calcite} : -1.22 to -0.22).
218 These values evidence thermodynamically optimum conditions for locally constrained carbonate precipitation
219 and sulphate dissolution, leading to the concomitant existence of sulphated-rich inputs.

220 The Li^+ concentration in shallow brines ranges from 771 – 1,213 $mg\ L^{-1}$ in Olaroz and 442 – 1,739 mg
221 L^{-1} in Cauchari. The highest Li grade zones occupy the central area of these two salars (Fig. 7B and C). The
222 mean Li^+ concentration is 860 $mg\ L^{-1}$ in Cauchari and 1,014 $mg\ L^{-1}$ in Olaroz, the Li:Mg ratios are 0.86 and
223 0.89, respectively (Table 2). The borate concentration in these brines varies between 1,336 and 3,175 $mg\ L^{-1}$
224 (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
225 Cauchari and 0.29 in Olaroz.

226

227 *The Salinas Grandes*

228 Salinas Grandes is a large salt pan of 280 km^2 placed at 3,410 m a.s.l. between 23°33' - 23°45'S and
229 65°51' - 66°12'W (Fig. 3C). This salar developed south of the Las Burras alluvial fan, which separates the
230 Salinas Grandes salt pan from the Guayatayoc playa lake to the north. Permanent streams feeding the Salinas
231 Grandes include the San Antonio de los Cobres and the El Moreno Rivers. The southern catchment area of the
232 San Antonio de los Cobres River includes numerous hydrothermal springs, while the headwater area of the El
233 Moreno basin involves seasonal periglacial processes. Muddy salt shorelines associated to the mouth of the El
234 Moreno River are mainly developed along the south-eastern border of the salt pan. Quaternary alluvial deposits
235 cover the low lying areas and reach the foot of mountains. The metasedimentary basement and the Cretaceous to
236 Paleocene sedimentary sequences are the most widespread lithologies along the eastern side of the basin, while
237 Paleozoic and Mesozoic plutonic rocks outcrop in the west-boundary ranges.

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

243 the most diluted (conductivity = 233.85 mS cm⁻¹) and characterizes by the lowest Ca²⁺ concentration compared
244 with the remaining samples collected from the Salinas Grandes (Fig. 5), and a Na:Cl ratio ~1 (Fig. 6A).
245 **Conversely**, the sample SG7 contains high Mg²⁺ and K⁺ concentrations, even when compared with the other
246 salars of the Northern Puna (Fig. 5A). The Salinas Grandes brines also show nearly equivalent proportions of
247 Ca²⁺, Mg²⁺ and K⁺ with Ca:Mg ~1 (Fig. 4), and typically have Ca²⁺ > SO₄²⁻ (Fig. 6B). Saturation **indexes indicate**
248 that brines are undersaturated in calcite, aragonite, and dolomite (SI_{dolomite}: -2.07 and -1.55, SI_{aragonite}: -1.30 to -
249 1.11 and the SI_{calcite}: -1.15 and -0.97).

250 The equivalent concentrations of **Li** and borate through the salar are similar (Fig. 5A), with the Li:B
251 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
252 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
253 concentration of borate is from 309 and up to 542 mg L⁻¹, and Li⁺ ranges between 25 and 1,018 mg L⁻¹, with the
254 highest **Li** grade zone located at the western margin of the salar (Fig. 7D). The mean Li⁺ concentration is 332 mg
255 L⁻¹ and the mean Li:Mg ratio is 0.54 (Table2).

256

257 **DISCUSSION**

258 The major chemical composition of the studied brines is rather constant; most samples are of the Na/Cl⁻
259 type with some subordinated samples of the Na/Cl⁻-SO₄²⁻ type. Thus, the highly concentrated brines are typically
260 rich in Na⁺ and Cl⁻, and relatively poor in Ca²⁺, Mg²⁺ and HCO₃⁻ + CO₃²⁻. An additional common feature in the
261 Northern Puna brines is that K⁺ concentrations are from 2 to 6 times higher than those of Mg²⁺. However, the
262 most conspicuous feature is the high **Li** grades, with average concentrations from 82 to 1,014 mg L⁻¹, the highest
263 **ones found** in the Cauchari and Olaroz salt pans.

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

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

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

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

295 The hydrothermal activity is considered as one of the most significant factors for the formation of Li
296 and boron rich brines in the Central Andes (Risacher et al. 2003; Godfrey et al. 2013; López Steinmetz 2017; and
297 references therein). Indeed, a number of authors indicated that the main sources of Li in Uyuni and the nearby
298 salars of Coipasa and Empexa in the southern part of the Bolivian Altiplano are thermal springs associated with
299 Quaternary rhyolitic volcanism (Shcherbakov and Dvorov 1970; Ericksen et al. 1977; Campbell 2009). Since
300 hydrothermal activity on the region is largely related to volcanism and the formation of the plateau (i.e., Isacks
301 1988; de Silva 1989; Allmendinger et al. 1997; McQuarrie et al. 2002; Kay et al. 2010; Perkins et al. 2016; and

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

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

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

327 In order to compare the relative abundance of ionic species in different salars, or between samples from
328 the same salar with uneven salinities, it is necessary to remove the effect of the evaporative concentration. The
329 relative abundance of Ca^{2+} , Mg^{2+} , K^+ , Li^+ and BO_3^{3-} in salars from the Northern Puna is presented in Figure 9. In
330 this diagram, the evaporative effect was removed by employing TDS (total dissolved solids, for TDS method see
331 [caption of Fig. 9](#)) normalized values. This diagram is substantially different from Figure 5 where plotted data

332 involve absolute ionic concentrations (the amount of ionic species that could be obtained from one litre of brine).
333 Normalized concentrations revealed that the four salars contain similar proportions of Ca^{2+} , the Salinas Grandes
334 brines are proportionally richer in K^+ and BO_3^{3-} , and the Salar de Cauchari contains proportionally higher Li^+
335 concentrations than its neighbour Northern Puna salars (Fig.8). This suggests that if a brine sample from the salar
336 de Jama (which is less saline than brines from Cauchari) is hypothetically evaporated in order to increase its
337 salinity up to the values of Cauchari, then, one litre of the Jama brine would still have a lower Li grade than the
338 same volume of the Cauchari brine. Consequently, the evaporative concentration process of such brines would
339 be more efficient for Li recovering at Cauchari than Jama. This statement seems an evident matter when
340 comparing Cauchari and Jama's brines because the mean Li^+ concentration of Cauchari is 860 mg L^{-1} and that of
341 Jama is 82 mg L^{-1} (Table 2). However, the extrapolation of this rule to the other salars of the Northern Puna (Fig.
342 9) allows stating that the evaporative concentration process in Cauchari is more efficient than in Olaroz (even if
343 the mean Li^+ concentration of the latter reaches $1,014 \text{ mg L}^{-1}$ versus 860 mg L^{-1} of the former).

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

354 Economically viable Li-rich brines in the Central Andes contain varying amounts of the major cations
355 and anions (Na^+ , K^+ , Mg^{2+} , Ca^{2+} , Cl^- , SO_4^{2-} , and CO_3^{2-}), which can form a wide range of ionic brine
356 compositions. In general, the Northern Puna's brines contain less Mg^{2+} than those accumulated in Atacama and
357 Uyuni (Fig. 8B). Nonetheless, the extremely high Li^+ concentration of Atacama remains the most important
358 difference between all these salars (Table 2). An additional and substantial difference is the oversized surface of
359 Uyuni and Atacama compared with the dimension of the Northern Puna salars. These two aspects, the Li^+
360 concentration and the salar size, are potentially limiting the whole resources of the Northern Puna salt pans.

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

363

364 **Conclusion**

365 This study reports the results of a regional Li exploration campaign covering an area of 9,000 km² in the
366 Northern Puna that included the four major salars in the region. These evaporite systems represent remarkable Li
367 prospects with mean Li⁺ concentrations varying between 82 and 1,014 mg L⁻¹, and mean Li:Mg ratios ranging
368 from 0.92 to 0.54.

369 The major chemical composition of the studied brines is rather constant; most samples are of the Na/Cl
370 type with some subordinated samples with a major ionic composition of the Na/Cl-SO₄²⁻ type, and with K>Mg.
371 Evaporative concentration, dissolution/precipitation of halite and gypsum/anhydrite, and the precipitation of
372 calcite/aragonite/dolomite are important processes controlling the major chemical composition of brines. Unlike
373 major ions, the concentrations of minor elements such as Mg²⁺, Li⁺ and BO₃³⁻ do not show clear correlation with
374 salinity, which suggest that some other factors are controlling their spatial distribution in the shallowest brines of
375 the studied salars. The absence of a geographical/geomorphological pattern for the ionic concentrations suggests
376 that the hydrochemistry of salars is being partially conditioned by local and regional intrinsic characteristics of
377 each basin, as well as by regional features related to the geological/tectonic nature of the Andean Plateau. These
378 characteristics are likely responsible for the higher Li concentrations in the N-S depression occupied by the
379 Olaroz and Cauchari salars compared with the neighbour salars located towards the margins of the northern Puna
380 region.

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

386

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581 **Figure captions**

582

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

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

598

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

602

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

605

606 Fig. 5. Comparative concentrations of Ca²⁺, Mg²⁺, K⁺, Li⁺ and BO₃³⁻ (A) and electrical conductivity (B) of
607 samples collected from the Salar de Jama (JA), Olaroz (OL), Cauchari (CA) and Salinas Grandes (SG).

608

609 Fig. 6. Scatter diagrams showing the variation of Na⁺ versus Cl⁻ (A) and Ca²⁺ versus SO₄²⁺ (B and C) in the
610 studied brines. Abbreviations are: Jama (JA), Olaroz (OL), Cauchari (CA), Salinas Grandes (SG), Guayatayoc
611 (G), Hombre Muerto (HM), Uyuni (UYU) and Atacama (ATA). The HM data were taken from Godfrey et al.
612 (2013). The UYU samples UB and UE and the ATA data set are from Risacher and Fritz (2009). The UYU
613 samples 109, 128 and 120 were taken from Ericksen et al. (1977). The G samples are from Lopez Steinmetz
614 (2017) and samples JA, OL, CA and SG are from this contribution. The HM samples 10, 11 and 12 are lagoon
615 brines, sample 13 is a brine collected at 200 cm depth in a hole drilled into the salar (Godfrey et al. 2013). The
616 UYU samples UB and UE correspond to brines collected at 100 cm depth (Risacher and Fritz 2009), sample 109
617 was collected in a brine pool and samples 120 and 128 are brines collected from holes drilled 40 to 50 cm into
618 the salt crust (Ericksen et al. 1977). Samples GG₃, GG₄ and GQ₀ were collected from pits dug in the playa lake
619 sediments (Lopez Steinmetz 2017).

620

621 Fig. 7. Li grade zones in the four major salars of the Northern Puna Plateau. Brine Li concentrations are in mg L⁻¹.
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623

624 Fig. 8. Scatter diagrams showing the variation of (Na⁺+Cl⁻) and Conductivity with Li⁺ (A) and Li⁺ versus Mg²⁺
625 (B and C) in the studied brines. Jama (JA), Olaroz (OL), Cauchari (CA), Salinas Grandes (SG). Data

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

628

629 Fig. 9. Comparative Ca^{2+} , Mg^{2+} , K^+ , Li^+ and BO_3^{3-} concentration ranges of samples collected from the Salar de
630 Jama (JA), Olaroz (OL), Cauchari (CA) and Salinas Grandes (SG). The TDS value was obtained from electrical
631 conductivity, by employing a conversion factor of 1 (TDS = Conductivity) based on the relation between the
632 concentration of all the analysed ions relative to conductivity (Fig. A of the electronic supplementary material).

633

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

636

637 Table 2. Comparative attributes of the Northern Puna's salars and Atacama, Uyuni and Hombre Muerto. The
638 mean Li^+ concentration and Li:Mg ratios of Jama, Olaroz, Cauchari and Salinas Grandes were settled based on
639 original data from this contribution (Table 1). The mean Li^+ concentration and Li:Mg of Guayatayoc correspond
640 to the mean value of the 3 brine samples (samples G3, G4 and Q0) reported in Lopez Steinmetz (2017). The
641 mean Li^+ concentration reported for Atacama are from Ide and Kunasz (1989) and Kunasz (2006), and the mean
642 Li:Mg corresponds to values reported by COCHILCO (2013). The mean Li^{+a} concentration and Li:Mg^a ratio in
643 Uyuni corresponds to the mean values of 38 samples (from sample 100 to sample 133 and samples 146, 147 and
644 147A) reported by Ericksen et al. (1977). The mean Li^{+b} concentration and Li:Mg^b ratio corresponds to the
645 mean values of the 164 samples (from sample UA to sample RZ) reported by Risacher and Fritz (1991). The
646 mean Li^{+c} concentration and Li:Mg ratio of Hombre Muerto correspond to the mean value of the 9 samples
647 (samples 4, 5, 6 and 9 to 14) reported by Godfrey et al. (2013). The mean Li^{+d} concentration in Hombre Muerto
648 corresponds to the mean Li^+ concentration of 100 cm-deep brines reported by Garrett (2004) and Kesler et al.
649 (2012).