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1 **Lithium and Brine Geochemistry in the Salars of the Southern Puna,**
2 **Andean Plateau of Argentina**

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4 Romina Lucrecia López Steinmetz ^{1*}, Stefano Salvi ², Carisa Sarchi ¹, Carla Santamans ¹,
5 Lorena Cecilia López Steinmetz ³

6
7 ¹ *CONICET (INECOA), Instituto de Geología y Minería, Universidad Nacional de Jujuy, Av.*
8 *Bolivia 1661, S.S. de Jujuy 4600, Argentina*

9 ² *Université de Toulouse, CNRS, GET, IRD, OMP, 14 Av. Edouard Belin, Toulouse 31400,*
10 *France*

11 ³ *Instituto de Investigaciones Psicológicas (IIPsi-UNC-CONICET), Universidad Nacional de*
12 *Córdoba, Boulevard de la Reforma y Enfermera Gordillo s/n., 2do piso, Córdoba 5000,*
13 *Argentina*

14 * *corresponding author: lucrecialopezsteinmetz@hotmail.com*

15
16 **Abstract**

17 The Andean plateau is a small region of South America extending between northwest
18 Argentina, southwest Bolivia and northern Chile. It concentrates the largest global resources of
19 lithium brines in its numerous salars. Of these, the giant salars in Bolivia and Chile have been
20 relatively well studied, however, only little is known about the smaller, but numerous salars in
21 the Argentine Puna region. In this article, we present the results of the first regional-scale
22 reconnaissance exploration of the twelve major salars situated in the southern part of the Puna
23 plateau (24°S - 26°30'S). Hydrochemical data indicate that shallowest brines are characterized
24 by highly variable Li concentrations, with mean Li grades ranging between 57 and 570 mg L⁻¹,
25 and mean Li:Mg ratios from 0.01 to 1.24. A survey of the brine chemistry of the salars across

26 the Puna plateau, including its northern part, has revealed the absence of geographical pattern
27 in Li⁺ grade distribution. However, a comparison among mean Li⁺ grades, Li⁺:Mg²⁺ ratios, and
28 the size of all salars allows an estimation of their Li mining potential. Specifically, the salt pan
29 of Arizaro represents the high potential mainly due to its size; Antofalla-Botijuelas has a large
30 surface and promising Li:Mg ratios for Li recovering via brine evaporation, though its elongated
31 shape is a constraint; Pastos Grandes, Pozuelos, and Rincón have encouraging Li grades,
32 interesting salar sizes, and relatively easy access. Olaroz, Cauchari, and Hombre Muerto contain
33 the highest Li⁺ grades in brines of all of the Argentine Puna, and embody the most interesting
34 perspectives of the Argentine plateau and in a regional context. Salar sizes could be related to
35 maximum Li⁺ grade of brines. Larger salars would be then expected to contain higher Li⁺ grade
36 brines than smaller ones, which could be considered as a useful criterion for surveys of brine-
37 type deposits.

38 **Keywords:** lithium triangle; salt pan; Central Andes; hydrochemistry

39

1. Introduction

40 Within the past few years, it has become apparent that the global need for an energy
41 transition from fossil fuels depends not only on our capacity to come up with a renewable source
42 of energy, but also on our ability to store it. The success of Li-ion batteries, with early
43 applications in mobile electronics and now increasingly in electric and hybrid vehicles, has
44 caused batteries to become the prime source of Li consumption, worldwide. This has spurred a
45 renewed interest on lithium as a resource, to the point that it is now considered one of the most
46 critical materials of our times (e.g., Hache et al., 2018; Olivetti et al., 2017; Ghadbeigi et al.,
47 2015). One of the principal sources of lithium is the mineral spodumene (along with petalite
48 and lepidolite), found mainly in highly evolved pegmatites, with Australia being its largest
49 producer (mainly from Greenbush; Kesler et al., 2012). Processing, however, is carried out
50 mostly in China, which is also the world's largest consumer of this metal (Sun et al., 2017).
51 Another abundant source of lithium is the dissolved salt in modern brine deposits found in
52 evaporated altitude lakes, known as salars. The Andean plateau, located between Bolivia, Chile
53 and Argentina (also known as the lithium triangle), hosts numerous salars, and the region
54 contains more than 50% of the global Li resources (Munk et al., 2016). This form of lithium is
55 more easily processed than hard rock, causing Chile to become the largest exporter of the
56 finished product, lithium carbonate (Sun et al., 2017; Hache et al., 2018). This resource
57 represents therefore a strategic supply of lithium for the western world.

58 The largest known Andean salar is the giant Uyuni salar (10,580 km²) in Bolivia
59 (Ericksen and Salas, 1977; Risacher and Fritz, 1991), although this country is not a producer.
60 Second in size is the Salar de Atacama in Chile, which, with its 3,000 km² at mean grades of
61 1,400 mg L⁻¹, is the most important lithium resource in the world (Ide and Kunasz, 1989;
62 Kunasz, 2006). Argentina also has an enormous potential for lithium brine resources, with
63 sixteen of the remaining major salars located in this country's portion of the Andean plateau,

64 known as the Puna region (Fig. 1). The Puna plateau is divided into northern and southern parts.
65 The Northern Puna (located between *ca.* 22-24°S) hosts the salars of Guayatayoc, Salinas
66 Grandes, Olaroz, Cauchari, and Jama, which range in size between 25 and 280 km² and contains
67 brines ranging between about 80 and 1,000 mg L⁻¹ in mean Li⁺ concentrations (López
68 Steinmetz, 2017; López Steinmetz et. al., 2018; García et al., 2019). Among these salars, Olaroz
69 and Cauchari have the highest Li⁺ grades (means of 1,014 mg L⁻¹ and 860 mg L⁻¹, respectively),
70 and are presently being mined. Although the twelve salars in the Southern Puna plateau (south
71 of 24°S; Fig. 1) constitute a huge resource, only the Salar de Hombre Muerto is being currently
72 operated. All of these salars have been staked for mining rights, however very little is known
73 of the brine hydrochemistry of the Southern Puna's salars, except that mean Li⁺ grades of 520
74 and 400 mg L⁻¹ have been reported for Hombre Muerto (Garret, 2004; Kesler et al., 2012;
75 Godfrey et al., 2013) and Rincón (Ovejero Toledo et al., 2009), respectively, and an isotopic
76 data set is available for the Salar de Centenario and Ratones (Orberger et al., 2015).

77 This manuscript reports the outcome of a large effort to obtain data from the 12 major
78 salars scattered throughout the very remote Southern Puna region. It is the result of a two-year
79 regional exploration campaign carried out by the CONICET and the Institute of Geology and
80 Mining of the Jujuy University of Argentina. Along with the information previously reported
81 by López Steinmetz (2017) and López Steinmetz et al. (2018) on the northern Puna salars, its
82 aim is to contribute to knowledge of the hydrochemistry of the Andean salars, and to complete
83 the first broad survey of Li-bearing salars hosted on the Argentine plateau. This study concludes
84 the Li survey and brines chemistry characterization of Andean salars, offering for the first time
85 an overview of the true potential of the Andean Lithium Triangle.

86

87

2. Geology of the Study Area

88 The Southern part of the Puna plateau extends from 24°S to 26°30'S and is bounded by
89 major volcanic peaks that mark the Chilean-Argentinian border, such as the Lullillaco (6,723
90 m a.s.l.), Socompa (6,031 m a.s.l.), and Rincón (5,594 m a.s.l.), and by the Luracatao Range to
91 the east (Figs. 2 and 3; cf. Alonso et al., 1984). The salars in this study are located in orographic
92 depressions along NE-SW trending ranges that formed during uplift of the Andes. The main
93 geology consists of Paleozoic basement units; these include: i) Ordovician metasediments
94 (Copalayo, Caucota, and Falda Ciénaga formations; Turner, 1960; Aceñolaza, 1973),
95 submarine volcanic rocks (Schwab, 1973; Coira, 1979), riodacites, granites (Eastern Puna
96 Eruptive Belt, Taca-Taca, Macón, Arita, and La Casualidad; Méndez et al., 1973; Turner and
97 Méndez, 1979; Méndez et al., 1979); ii) Devonian marine sandstones (Salar del Rincón
98 Formation); iii) Carboniferous continental sandstones (Cerro Oscuro Formation); and iv)
99 Permian marine limestones (Arizaro Formation; Aceñolaza et al., 1972; Donato and Vergani,
100 1985; Galli et al., 2010).

101 Middle Eocene to upper Pliocene continental sedimentary rocks (Pastos Grandes Group;
102 Turner, 1960; Alonso, 1986; Alonso et al., 1991) are exposed along the Calalaste and Los
103 Colorados Ranges (Fig. 2A). Large areas of the Southern Puna are covered by upper Oligocene
104 - Pliocene dacites, andesites, ignimbrites, and Quaternary basalts (Salfity et al., 1984; Alonso
105 and Viramonte, 1987; Jordan and Alonso, 1987; Montero López et al., 2015; Maro et al., 2017).
106 Quaternary fine-grained sediments of alluvial origin cover the planes between the mountain
107 ranges. Salt pans form on low-laying areas because of the extreme climatic conditions that
108 prevail in these high-altitude endorheic basins (cf. López Steinmetz and Galli, 2015).

109

110

3. Methods

111 Between 2014 and 2017, 6 expeditions were run to the Southern Puna of Argentina in
112 order to sample residual brines from the twelve major salars in this region. These are the Salar

113 de Centenario (CE), Diablillos (DI), Hombre Muerto (HM), Incahuasi (IN), Pastos Grandes
114 (PG), Pozuelos (PZ), Ratones (RA), Antofalla-Botijuelas (AN), Arizaro (AR), Pocitos-Quirón
115 (PC), Rincón (RI), and Río Grande (RG, Figs. 2 and 3). Precise sample location is provided in
116 Table A1 of the Appendix. Most samples were collected in pits that were hand-dug in the salars,
117 at depth intervals of 40 to 90 cm, plus a number that were taken directly from brine pools
118 (samples CE1, CE2, DI3 to DI5, PG1 to PG3, PG5, PZ1, PZ5, PZ7, PZ8, AN1, AN2, PC1 to
119 PC4, and RI 5). Samples were stored in pre-cleaned, 2-L polyethylene bottles and kept at 5°C
120 in the field. No acidification was employed after sample collection. Samples were transported
121 directly to the laboratory after collection.

122 All samples collected in the twelve salars were analyzed at the Agua de Los Andes S.
123 A. laboratory (Jujuy, NW Argentina) and the resulting data are shown in Table 1. Values for
124 pH and electrical conductivity were determined with a Hanna HI2314 multi-range conductivity
125 meter. The calibration of the meter involved several steps. 1) Verification of the temperature
126 reading; 2) calibration of the conductivity meter using a 1,000- $\mu\text{S}/\text{cm}$ calibration standard, to
127 obtain a conductivity cell constant of 5.0 \pm 0.5; and 3) calibration of the pH meter using buffer
128 solutions for pH 7 and 4, to obtain a slope comprised between 55 and 60 mVs. Salinities are
129 expressed as the total dissolved solids (TDS; mg L^{-1}), which were obtained by employing a
130 conversion factor of 0.50 on the measured electrical conductivity. This conversion factor
131 corresponds to the ratio observed between the measured electrical conductivity of samples and
132 their total analytical ionic concentrations (i.e., the sum of measured cations and anions). The
133 major ion composition was determined following the procedure outlined by Clesceri et al.
134 (1998). Concentrations of calcium (Ca^{2+}) were obtained by titrating with a 0.01 M EDTA
135 solution for the former, while those of magnesium (Mg^{2+}) were calculated by subtracting the
136 calcium concentration to the total hardness. Titration with a 0.01-N sulfuric acid solution was
137 employed to determine carbonate and bicarbonate ion (HCO_3^- and CO_3^{2-}) concentrations, using

138 methyl-orange and phenolphthalein, respectively, as end-point indicators. Chloride (Cl^-) was
139 measured by titration using the argentometric method. Concentrations of sulfate (SO_4^{2-}) were
140 determined by turbidimetry on the precipitate obtained by mixing it with BaCl_2 in an acetic acid
141 medium. Atomic Emission Spectroscopy was employed to analyse sodium (Na^+), potassium
142 (K^+) and lithium (Li^+) while boron (B) was determined by colorimetry using a carmine reactive.
143 Ion balance values were $\leq 10\%$ in all cases (cf. Fig. A1 and Table A2, Appendix).

144

145 **4. Li-Bearing Salars of the Southern Puna**

146

147 *4.1. Salar de Centenario (CE, east)*

148 Centenario is a 7-km² playa lake located at 3,816 m a.s.l., between the Los Colorados,
149 Pastos Grandes, and Luracatao Ranges (Fig. 2). Centenario also includes 70 km² of saline
150 muddy shore zones, which are fed by the Singuel, Ciénaga Grande, and Copalayo rivers.

151 Brines collected in the Salar de Centenario are alkaline, with pH values comprised
152 between 7.50 and 7.70, and TDS ranging between 26,090 and 48,590 mg L⁻¹ (Table 1).
153 According to their major chemical composition, brines are of the $\text{Na}^+ / \text{Cl}^- - \text{SO}_4^{2-}$ type, with
154 high SO_4^{2-} , relatively abundant K^+ and Mg^{2+} , and are depleted in Ca^{2+} (Fig. 4). No correlation
155 between major ions has been identified, with the exception of sample CE4, whose $\text{Na}^+:\text{Cl}^-$ ratio
156 $\sim 1:1$ reflects equilibrium solubility of halite (Fig. 5).

157 The Li^+ concentration in the Salar de Centenario ranges between 25 and 377 mg L⁻¹,
158 with a mean Li^+ concentration of 141 mg L⁻¹. Positive correlations could exist between the Li^+
159 concentrations and those of K^+ , B, and Mg^{2+} (Fig. 6). The mean Li:K ratio is 0.37 while the
160 mean Li:Mg ratio is 0.20 (Table 2). Boron concentrations range between 277 and 581 mg L⁻¹,
161 and the mean Li:B ratio is 0.97.

162

163 4.2. Salar de Diablillos (DI, east)

164 Diablillos is a 4-km² playa lake located at 4,032 m a.s.l., between the Los Colorados,
165 Luracatao and Pastos Grandes Ranges (Fig. 2). Muddy shore zones covering about 29 km² at
166 the mouth of the Diablillos river, to the east, are also considered as part of the Salar de
167 Diablillos.

168 The Diablillos brines are alkaline, pH is 8.00, and TDS values range between 26,350
169 and 80,735 mg L⁻¹ (Table 1). According to their major chemical composition, brines are of the
170 Na⁺ / Cl⁻ - SO₄²⁻ type, with high SO₄²⁻, with relatively abundant K⁺ and Mg²⁺ (Fig. 4). The ~1:1
171 ratio between Na⁺ and Cl⁻ in samples DI3 and DI4 indicates the dissolution of halite. Brines are
172 also characterized by SO₄²⁻ > Ca²⁺ > CO₃²⁻+HCO₃⁻ (Fig. 5).

173 The Li⁺ concentration in the Diablillos's brines ranges between 47 and 357 mg L⁻¹, with
174 a mean Li⁺ concentration of 180 mg L⁻¹. The mean Li:K ratio is 0.26 and the mean Li:Mg =
175 0.26 (Table 2). Boron concentrations are up to 808 mg L⁻¹, with a mean Li:B ratio of 0.86.

176

177 4.3. Salar de Hombre Muerto (HM, east)

178 The Salar de Hombre Muerto is located at 3,970 m a.s.l., between the Aguas Calientes,
179 Calalaste, Los Colorados, and Pastos Grandes Ranges, at the foot of the Ratones volcano (5,252
180 m a.s.l.) (Vinante and Alonso, 2006). Hombre Muerto is by far the largest salar among those of
181 the eastern part of Southern Puna. It spreads between 66°53'24" - 67°13'30"W and 25°13'48"
182 - 25°30'36"S (Fig. 2), and includes a 230 km² salt pan in the west, a 65 km² lagoon in the
183 eastern side, and a 245 km² playa domain that mainly develops in its northern reaches, for a
184 total area of 540 km². The main tributaries are the Ratones river to the north, and the Los Patos
185 river, sourced at the foot of the Galán volcano (5,919 m a.s.l.), which reaches this salar from
186 the southeast.

187 Brines from the Salar de Hombre Muerto are also alkaline, with pH values ranging
188 between 7.80 and 8.20, and TDS ranging between 31,215 and 205,022 mg L⁻¹ (Table 1).
189 According to their major chemical composition, they are of the Na⁺ / Cl⁻ type, with relatively
190 abundant K⁺ (Fig. 4). The concentrations Ca²⁺ and SO₄²⁻ in sample HM4 correspond to a
191 stoichiometric ratio of 1:1, a value that suggest dissolution of gypsum (Fig. 5).

192 Hombre Muerto contains the highest values of lithium in Southern Puna, with a mean
193 Li⁺ concentration of 570 mg L⁻¹ for a range between 85 and 1,013 mg L⁻¹. The highest grades
194 are found in the middle part of the salar. The mean Li:K ratio is 0.69, and the mean Li:Mg ratio
195 is 0.92 (Table 2). Boron concentrations range between 377 and 1,490 mg L⁻¹, and the mean
196 Li:B ratio is 1.90 (Fig. 6).

197

198 *4.4. Salar de Incahuasi (IN, east)*

199 Incahuasi is a playa lake with an elongated shape oriented north-south. It is situated
200 between the Calalaste and Morada mountain ranges, at an altitude of 3,269 m a.s.l. It is the
201 southernmost salar in the Puna region, spreading between 67°39'03" - 67°40'35"W and
202 26°18'44" - 26°28'30"S (Fig. 2). Its southern edges are covered by more than 33 km² of dune
203 fields. This salar includes two distinctive zones; north of 26°23'29"S is a saline, episodically
204 flooded part, covering about 18 km², while the 20 km² to the south consist of a saline muddy
205 playa lake. The salar is mostly fed by the Cortaderas river, coming in from the northeast.

206 Brines from the Salar de The Incahuasi are slightly alkaline, with a pH ranging between
207 6.70 and 7.30. TDS values range between 48,220 and 107,340 mg L⁻¹ (Table 1). According to
208 their major chemical composition, brines are of the Na - Mg²⁺ / Cl⁻ type, with high Mg²⁺, and
209 depleted in Ca²⁺ (Fig. 4). Major ratios are characterized by Cl⁻ > Na⁺, Ca²⁺ > SO₄²⁻, and Ca²⁺ >
210 CO₃²⁻+HCO₃⁻ (Fig. 5).

211 At Incahuasi, the Li^+ content in brines range between 22 and 145 mg L^{-1} , with a mean
212 of 95 mg L^{-1} . The highest concentrations of Li occur in the middle part of its saline, floodable
213 zone in the north. Brines from Incahuasi contain the highest concentrations of magnesium
214 among all of the salars that are located in the eastern part of the Southern Puna (Fig. 6). K^+ and
215 Mg^{2+} concentrations do not correlate with Li^+ concentrations (Fig. 6); the mean Li:K ratio is
216 0.09 while the mean Li:Mg ratio is 0.01 (Table 2). A positive correlation may exist between B
217 and Li^+ (Fig. 6). Boron concentrations range between 114 and 570 mg L^{-1} , and the mean Li:B
218 ratio is equal to 0.62.

219

220 4.5. Salar de Pastos Grandes (PG, east)

221 The Salar de Pastos Grandes is located at 3,780 m a.s.l. between the Los Colorados,
222 Pastos Grandes, and Japeler Ranges, between $66^{\circ}43'48''$ - $66^{\circ}39'18''\text{W}$ and $24^{\circ}31'30''$ -
223 $24^{\circ}36'18''\text{S}$ (Fig. 2). Pastos Grandes has a triangular shape and the salt pan zones cover 27 km^2 ,
224 to which must be added a 4.80 km^2 saline lake, located at its north-eastern margin. The main
225 tributaries are the Corral Colorado and Pastos Grandes rivers in the north, and the Ciénaga
226 Redonda river arriving from the east.

227 Brines from Pastos Grandes are alkaline, with pH values ranging between 8.00 and 8.30,
228 and TDS ranging between 154,030 and 226,600 mg L^{-1} (Table 1). According to their major
229 chemical composition, brines are of the $\text{Na}^+ / \text{Cl}^-$ type, with relatively abundant Mg^{2+} , and
230 depleted in Ca^{2+} (Fig. 4). When comparing these brines with those from the other salars, the
231 Pastos Grandes shows the highest concentrations of CO_3^{2-} and HCO_3^- . Near stoichiometric
232 trends between the $\text{Ca}^{2+} : \text{CO}_3^{2-} + \text{HCO}_3^-$ and $\text{Ca}^{2+} : \text{SO}_4^{2-}$ ratios likely reflect equilibrium
233 solubility of Ca-Mg sulfates and Ca-carbonates (Fig. 5). However, the fact that the linear trend
234 defined by the $\text{Mg}^{2+} : \text{SO}_4^{2-}$ data deviates from a 1:1 ratio reflects that Mg salts, like epsomite
235 ($\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$), are not in equilibrium with the brine.

236 The Li^+ concentrations in the Pastos Grandes's brines range between 305 and 857 mg
237 L^{-1} , with a mean of 483 mg L^{-1} . The highest Li grade zone in the eastern part of the salar. The
238 mean Li:K ratio is 0.82 while the mean Li:Mg ratio is 0.19 (Table 2). Boron concentrations
239 range between 300 and 812 mg L^{-1} , and the mean Li:B ratio is 2.24.

240

241 *4.6. Salar de Pozuelos (PZ, east)*

242 The salar de Pozuelos is a 75- km^2 salt pan with an oval shape along a NE-SW direction.
243 It is located at 3,663 m a.s.l. at the interior of the Los Colorados Range (Fig. 2). The main
244 tributary is the Pozuelos river to the north.

245 Brines from the Salar de Pozuelos are alkaline, with pH values ranging between 7.80
246 and 8.60, and TDS ranging between 205,243 and 298,574 mg L^{-1} (Table 1). According to their
247 major chemical composition, brines are of the $\text{Na}^+ / \text{Cl}^-$ type, with relatively abundant K^+ and
248 Mg^{2+} (Fig. 3). Major ratios are characterized by $\text{Cl}^- > \text{Na}^+$, $\text{SO}_4^{2-} > \text{Ca}^{2+}$, and $\text{Ca}^{2+} > \text{CO}_3^{2-}$
249 $+\text{HCO}_3^-$. Non-stoichiometric ratios were observed combining different major ion pairs ($\text{Cl}^- >$
250 Na^+ , $\text{SO}_4^{2-} > \text{Ca}^{2+}$, and $\text{Ca}^{2+} > \text{CO}_3^{2-}+\text{HCO}_3^-$), suggesting that the dominant ion concentrations
251 are independent of salt equilibrium solubility (Fig. 5).

252 In the Pozuelos's brines, Li^+ concentrations range between 75 and 940 mg L^{-1} with a
253 mean of 401 mg L^{-1} . Grades increase towards the central part of the salt pan. Stoichiometric 1:1
254 ratios are observed between Li^+ and K^+ in samples PZ5 and PZ6 (Fig. 6 A). The mean Li:K
255 ratio is 0.69, and the mean Li:Mg ratio is 0.43 (Table 2). Boron ranges between 202 and 2,102
256 mg L^{-1} , and the mean Li:B ratio is 1.26.

257

258 *4.7. Salar de Ratones (RA, east)*

259 Ratones is a north-south stretched playa lake located at 3,822 m a.s.l. between the
260 Colorados and Pastos Grandes - Luracatao Ranges. The playa lake surface covers only 3 km^2 ,

261 with most of the salar consisting of 47 km² of saline muddy shore zones, spread between
262 66°47'10" - 66°50'54"W and 25°02'42" - 25°11'42"S (Fig. 2). Main tributaries are the Singuel
263 and Quebrada Honda rivers.

264 Brines from the Salar de Ratones are alkaline and moderately saline, TDS values are
265 between 28,080 and 82,580 mg L⁻¹, and pH range between 7.50 and 7.80 (Table 1). According
266 to their major chemical composition, brines are of the Na⁺ / Cl⁻ - SO₄²⁻ type, with relatively
267 abundant K⁺ and Ca²⁺ (Fig. 4).

268 The Li⁺ concentration in the Ratones's brines range between 88 and 260 mg L⁻¹, and the
269 mean Li⁺ concentration of the three samples collected in the salt pan zone is 158 mg L⁻¹. The
270 Li⁺, K⁺ and Mg²⁺ mean ratios are: Li:K = 0.38, and Li:Mg = 1.24 (Table 2). Boron
271 concentrations range between 312 and 509 mg L⁻¹, and the Li:B ratio = 1.06.

272

273 4.8. Salar de Antofalla-Botijuelas (AN, west)

274 Salars in the western part of the Southern Puna are relatively large. The Salar de
275 Antofalla-Botijuelas covers some 655 km² with its elongated shape stretching N-S for more
276 than 100 km. This salt pan is at an altitude of 3,330 m a.s.l., between 25°24'54" and 26°06'54"S
277 at ca. 67°42'W (Fig. 3). The salar is delimited by the Calalaste and Antofalla Ranges and main
278 tributaries are the Archibarca, Antofalla, Aguas Calientes, and Aguas Dulces rivers. There are
279 abundant thermal springs around this salar, especially in the northern and central western
280 borders of the salar (Botijuelas thermal sources), and samples AN1, AN2, and AN3 correspond
281 to thermal waters sampled at temperatures of 31.50 °C.

282 Brines from the Salar de Antofalla-Botijuelas are only slightly alkaline, with pH values
283 comprised between 7.40 and 7.80, and TDS ranging between 9,110 and 184,570 mg L⁻¹ (Table
284 1). According to their major chemical composition, brines are of the Na⁺ / Cl⁻ - SO₄²⁻ type, with
285 relatively abundant Ca²⁺ and low Mg²⁺ (Fig. 4).

286 The Li^+ concentrations in this salar increase northwards, ranging between 46 and 615
287 mg L^{-1} , with a mean of 209 mg L^{-1} . Positive trends parallel to 1:1 are observed between the Li^+
288 concentrations and those of K^+ and Mg^{2+} (Fig. 6); the mean Li:K ratio is 0.90, and the mean
289 Li:Mg ratio = 0.64 (Table 2). Boron concentrations range between 415 and 878 mg L^{-1} , and the
290 mean Li:B ratio is 0.83.

291

292 4.9. Salar de Arizaro (AR, west)

293 Arizaro, also in western Southern Puna, is the largest salar in the Puna plateau and in
294 Argentina altogether. This salt pan covers an area of $1,708 \text{ km}^2$, between $67^\circ 18' 33''$ -
295 $68^\circ 02' 11''$ W and $24^\circ 20' 42''$ - $25^\circ 05' 44''$ S (Fig. 3). Arizaro is located at an elevation of 3,474
296 m a.s.l., and is bounded by the Archibarca and Antofalla ranges and by the volcanic peaks that
297 define the Argentinian border with Chile.

298 Brines from the Salar de Arizaro are alkaline, with pH values comprised between 7.30
299 and 7.40, and TDS ranging between 38,865 and $308,175 \text{ mg L}^{-1}$ (Table 1). According to their
300 major chemical composition, brines are of the $\text{Na}^+ - \text{K}^+ / \text{Cl}^- - \text{SO}_4^{2-}$ type, with relatively
301 abundant Mg^{2+} (Fig. 4). In addition of being the largest salar of the Argentinean plateau, Arizaro
302 contains the highest concentrations of K^+ , B, and SO_4^{2-} of the Southern Puna. No obvious
303 correlation could be observed among data for major ions (Fig. 5). A $\text{Mg}^{2+} : \text{SO}_4^{2-}$ linear trend
304 parallel to the 1:1 ratio indicates some degree of equilibrium solubility for Mg salts, like
305 epsomite ($\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$). However, trends parallel to the Na^+ and SO_4^{2-} axes suggest the
306 presence of other salts that are not in equilibrium with the brine.

307 The Li^+ concentrations in the Salar de Arizaro range between 52 and 465 mg L^{-1} , with
308 an increase towards the south-central part. Mean Li^+ concentrations for the whole salar are of
309 191 mg L^{-1} . The mean Li:K ratio is 0.24 while the mean Li:Mg ratio is 0.16 (Table 2). Boron
310 concentrations range between 380 and $3,382 \text{ mg L}^{-1}$, with a mean Li:B ratio of 0.28.

311

312 *4.10. Salar de Pocitos-Quirón (PC, west)*

313 The Salar de Pocitos-Quirón consists of a 50-km² saline system at an elevation of 3,663
314 m a.s.l. It is elongated north-south and lays between the Los Colorados and Calalaste Ranges
315 (Fig. 3). A 10-km long alluvial fan at the mouth of the Los Colorados river separates the Salar
316 de Pocitos to the north from the Quirón playa lake to the south. The Pocitos salt pan zone covers
317 28 km² and spreads between 67°00'18" - 67°03'36"W and 24°22'30" - 24°27'30"S. The Quirón
318 playa lake has a surface of 422 km² and spreads between 24°15'18" and 24°46'12"S. In addition
319 to the Los Colorados river, another important tributary is the Agua Blanca river that emerges at
320 the foot of the Quevar volcano (6,130 m a.s.l.).

321 Brines from the Salar de Pocitos-Quirón are alkaline, pH values range between 7.80 and
322 8.30, and salinity is high, with TDS ranging between 29,480 and 299,217 mg L⁻¹ (Table 1).
323 According to their major chemical composition, brines are of the Na⁺ - Ca²⁺ - Mg²⁺ / Cl⁻ - SO₄²⁻
324 type (Fig. 3). The Pocitos-Quirón brines contain the lowest concentrations of Li⁺, K⁺, Mg²⁺,
325 and B among all salars in the Southern Puna (Fig. 6).

326 Li⁺ ranges between 22 and 101 mg L⁻¹, with the highest grade zone occurring in the
327 central part of the Pocitos salt pan. The mean Li⁺ concentration is 57 mg L⁻¹, the mean Li:K
328 ratio is 0.26 and the mean Li:Mg ratio is 0.17 (Table 2). Boron concentrations range between
329 60 and 208 mg L⁻¹. A strong positive correlation between Li⁺ and B is observed along the
330 stoichiometric ratio 1:1 (Fig. 6 B), and the mean Li:B ratio of these brines is 1.37.

331

332 *4.11. Salar de Rincón (RI, west)*

333 The Salar de Rincón is a playa lake located at 3,725 m a.s.l., at the foot of the Tultul
334 (5,270 m a.s.l.), Rincón (4,530 m a.s.l.), and Incahuasi (5,690 m a.s.l.) volcanoes, next to the
335 borders between Northern and Southern Puna and the Chile-Argentina border (Fig. 3). The

336 Salar de Rincón spreads between 66°57'54" - 67°10'46"W and 24°03'54" - 24°12'23"S,
337 covering a surface of 250 km². Main tributaries to this salar include the Catua and Huaytiquina
338 rivers, both coming in from the north, causing a 170-km² saline muddy shore zone that spreads
339 up to 23°55'48"S.

340 Brines from the Salar de Rincón are alkaline, with pH ranging between 8.60 and 8.80,
341 and TDS values comprised between 140,265 and 284,650 mg L⁻¹ (Table 1). According to their
342 major chemical composition, brines are of the Na⁺ - K⁺ / Cl⁻ - SO₄²⁻ type, with relatively
343 abundant Mg²⁺ (Fig. 4). Major ion concentrations are more elevated in the central part of the
344 salar. Samples along the Na⁺ and Cl⁻ stoichiometric 1:1 ratio suggest equilibrium solubility of
345 halite. Other major ionic ratios are characterized by SO₄²⁻ > Ca²⁺ and Mg²⁺, and Ca²⁺ > CO₃²⁻
346 +HCO₃⁻ (Fig. 5). Linear trends parallel to the SO₄²⁻ axis indicate that the concentrations of Ca²⁺
347 and Mg²⁺ are not controlled by equilibrium solubility of salts (Fig. 5).

348 Lithium ion concentrations in the Rincón's brines range between 112 and 651 mg L⁻¹,
349 with the highest-grade zone occurring in the central part of the salar, and the mean Li⁺
350 concentration being 281 mg L⁻¹. Positive linear trends are observed between Li⁺ and Mg²⁺ (Fig.
351 6); the mean Li:K ratio is 0.25 while the mean Li:Mg ratio is 0.24 (Table 2). Boron
352 concentrations range between 1,405 and 2,098 mg L⁻¹ and the mean Li:B ratio is 0.45.

353

354 4.12. Salar de Río Grande (RG, west)

355 The Salar de Río Grande is a 176-km² elliptically-shaped saline system, oriented north-
356 south, occurring at an altitude of 3,668 m a.s.l. between 68°07'22" - 68°12'07"W and
357 24°59'24" - 25°06'18"S (Fig. 3). The surface of the salt pan zone covers 56 km², with remaining
358 of the salar consisting of a 120 km² saline muddy playa lake that extends to the south of the
359 salar, to 25°10'55"S. The main tributary is the Río Grande river, which contains some
360 hydrothermal springs in its southernmost headwaters.

361 Brines from the Salar de Río Grande are highly saline and characterized by TDS values
362 between 199,070 and 284,605 mg L⁻¹. These brines are neutral to slightly alkaline, with pH
363 ranging between 7.00 and 7.20 (Table 1). According to their major chemical composition,
364 brines are of the Na⁺ / Cl⁻ - SO₄²⁻ type, with similar proportions of K⁺, Mg²⁺ and Ca²⁺ (Fig. 4).
365 Río Grande contains the highest concentrations of Ca²⁺ and SO₄²⁻ of the Southern Puna (Fig. 5
366 B). Linear trends parallel to the SO₄²⁻ axis indicate that the concentrations of Ca²⁺ and Mg²⁺ are
367 not controlled by equilibrium solubility of salts (Fig. 5).

368 The concentrations of Li⁺ range between 139 and 692 mg L⁻¹, with the highest Li grade
369 measured in the central part of the salar. The mean Li⁺ concentration is 396 mg L⁻¹. Positive
370 linear trends, parallel to the Li⁺ axis, suggest that there is no obvious correlation among Li, K⁺,
371 and B. However, a stoichiometric linear trend is observed between Li⁺ and Mg²⁺ (Fig. 6). The
372 mean Li:K ratio is 0.72 while the mean Li:Mg ratio is 0.33 (Table 2). Boron concentrations
373 range between 303 and 545 mg L⁻¹, the mean Li:B ratio = 2.81.

374

375 5. Discussion

376

377 5.1. Classification of brines in the regional context

378 There are a number of common features that can be distilled from the major chemistry
379 of the brines investigated in this study (Fig. 4). The first observation is that they are all rich in
380 Na⁺ and Cl⁻ and that, at least for most brines, concentrations of K⁺ (e.g., HM, RA, AR, RI) and
381 Mg²⁺ (e.g., IN, PG, AR) are relative important. There are also important differences among the
382 brines of these salars. For instance, DI, PC and AN show wide variations in the proportions of
383 most cations, while RG, RI, IN, HM, and CE have relatively constant values across the salar.
384 In general, with the exception of RA, salars located in the western side of the Southern Puna
385 are richer in Ca²⁺ than those in the eastern side, which in turn, are relatively enriched in Mg²⁺.

386 The concentration of SO_4^{2-} in western salars is generally higher than that in the eastern side,
387 representing intermediated values between the latter (lower SO_4^{2-}) and the salars from Northern
388 Puna studied by López Steinmetz et al. (2018) (higher SO_4^{2-}). Another remarkable difference
389 between Southern and Northern Puna is a clearly higher concentration of Mg^{2+} in the southern
390 salars. These ionic patterns could be related to the characteristics of lithologic substrates. The
391 basement rocks differ between the southern and northern portion of the Puna plateau: while
392 Ordovician metasedimentary sequences predominate in the north, a metamorphic-magmatic
393 basement (biotite gneiss, felsic granulites) prevails in the south (Lucassen et al., 2011;
394 Bahlbourg et al., 2016; Egenhoff and Lucassen, 2003). Cenozoic andesitic and dacitic
395 ignimbrites, associated with Miocene - Pliocene caldera complexes, largely cover the northern
396 part of the Argentine Puna (particularly between $22^{\circ}30'$ - 23° S), whereas they are less abundant
397 towards the south (de Silva, 1989; Caffè et al., 2002; Schnurr et al., 2007; Kay et al., 2010;
398 Grosse et al., 2017, 2018; Montero López et al., 2015). Conversely, although mafic volcanism
399 does occur in the North, the Southern Puna is characterized by a large number of Miocene-to-
400 Quaternary mafic monogenic volcanoes (285 centers; Barcelos Haag et al., 2019), which are
401 typically formed of Mg-rich basaltic andesites (Maro et al., 2017a). They are characterized by
402 more primitive compositions than those in the north (Maro et al., 2017b). Lavas with more
403 alkaline compositions (i.e., basaltic trachyandesites with near shoshonite compositions) are rare
404 across the Puna, and occur mostly towards the eastern side of this region (Maro & Caffè, 2013).
405 It is thus possible that the higher Mg^{2+} concentrations in the Southern Puna's salars are a
406 consequence of weathering (and alteration?) of mafic rocks, whereas the sulfate increase in the
407 Northern Puna probably derives from the Ordovician metasedimentary sequences. This is
408 consistent with observations by López Steinmetz (2017) concerning the Guayatayoc salar area,
409 who suggested that weathering of certain sections of the Ordovician basement (Santa Rosita
410 Formation; Turner, 1960; Moya, 1988) made of marine mudstones, fine-grained silty

411 sandstones, and shales (Buatois and Mángano, 2003) caused releasing of abundant SO_4^{2-} (López
412 Steinmetz, 2017).

413 The data presented above indicates that the chemistry of most brines evolves through
414 the sulfated pathway, with only a minor portion of samples passing through the calcic-sulfated
415 way (Hardie and Eugster, 1970; Fig. 7). Among our samples, the brines from IN stand out by
416 having the highest concentration in Mg^{2+} (Figs. 4A and 5C), while the remaining samples
417 evolve through the calcic pathway, given that they are Ca^{2+} and Mg^{2+} rich with respect to CO_3^{2-}
418 and SO_4^{2-} . Based on the above observations, one can outline a relationship between the
419 chemistry of brines that evolve through the calcic pathway and the local geology (Fig. 2 A): i)
420 the high concentrations of Mg^{2+} that characterize brines from Incahuasi are probably related to
421 the Cerro Oscuro Formation (consisting of continental red beds; Galli et al., 2010), which
422 outcrops in the ranges just east of this salar (note that there are no monogenic volcanoes - i.e.,
423 Mg-rich basaltic andesites - just next to Incahuasi; Fig. 2); ii) the ionic proportions of $\text{Ca}^{2+} +$
424 $\text{Mg}^{2+} > \text{CO}_3^{2-} + \text{SO}_4^{2-}$ generally correspond to samples that were collected adjacent to outcrops
425 that dominated by Quaternary sedimentary and volcanic rocks. In contrast, salars having brines
426 that evolve through the sulfated pathway are adjacent to basement sequences consisting mostly
427 of intrusive and volcanic units. This strongly suggests an igneous source for the sulfur, although
428 some SO_4^{2-} was probably released from weathering of metasediments.

429 In the five western salars, the decreasing order of average salinity is $\text{AR} \geq \text{PC} \geq \text{RG} \geq$
430 $\text{RI} \geq \text{AN}$ (Fig. 8). The concentrations of Ca^{2+} , Na^+ , K^+ , B, and Li^+ decrease according to $[\text{RG},$
431 $\text{RI}, \text{AR}] \geq [\text{AN}, \text{PC}]$. In the seven eastern salars, the decreasing order of average salinity is PZ
432 $\geq \text{PG} \geq \text{HM} \geq \text{IN} \geq \text{DI} \geq \text{RA} \geq \text{CE}$. In addition to salinity, the magnitude of Na^+ , Li^+ , Cl^- , and
433 B concentrations can be summarized by $[\text{PZ}, \text{HM}, \text{PG}] \geq [\text{RA}, \text{DI}, \text{CE}, \text{IN}]$. Although this
434 pattern is valid, there are local variations and there is no recognizable concentration pattern for
435 the remaining ions. According to the above, there would be no spatial (i.e., geographic)

436 correlation with the ionic concentrations of these elements nor with Li^+ . Nonetheless, as
437 mentioned previously, the concentrations of SO_4^{2-} , and in a lesser extent also those of Mg^{2+} , do
438 follow spatial patterns.

439

440 *5.2. Li concentration patterns*

441 Variations in the grades of Li in the brines of these salars can be assessed by plotting
442 Li^+ concentration against salinity and other conservative solutes such as Na^+ in the brines.
443 Figure 9 shows a general correlation for these parameters. This pattern is consistent with the
444 incompatible geochemical behaviour of Li, i.e., it becomes enriched in the residual brine during
445 salar evolution, a proxy of which is an increase in salinity. Another remarkable correlation can
446 be observed between maximum Li^+ grades measured in brines and salar size (Fig. 10). This
447 pattern is common to all of the salars studied in Argentina, including those from the Northern
448 Puna (López Steinmetz et al., 2018). The best correlations can be observed among salars with
449 surfaces smaller than about 400 km^2 . These show two positive trends: i) the Guayatayoc - RI -
450 Salinas Grandes - HM trend, represented by a regression line with a linear correlation (R;
451 Pearson correlation coefficient) of 0.80; and ii) the IN, RA, JA, DI, CE, RG, PG, PZ, OL, and
452 CA salars, which follow a linear trend characterized by $R = 0.84$. This feature suggests a
453 relationship between Li^+ grade and salar size, in addition to, of course, other major determining
454 factors that have been pointed out by Munk et al. (2016), such as the existence of Li supplying
455 sources, hydrological isolation, aridity, etc. A clear trend between Li^+ grade and salar size exists
456 for the smaller salars, while those of AR, AN and PC do not show as good a correlation, most
457 likely because their surfaces are much larger (up to three orders of magnitude), over diluting
458 the effect. Accordingly, larger salars would be expected to contain higher Li^+ grade brines than
459 smaller ones, which provides a useful criterion for the surveying of brine-type deposits.

460 The correspondence between the maximum Li^+ grades and salar sizes could be
461 indicative of the importance of basin scale processes such as rock weathering, isolation and
462 evaporation. In this sense, it is important to note that it has been recently shown that brines in
463 Atacama formed in a near surface setting, through geochemical processes including low-
464 temperature weathering, evaporation, formation of transition zone brines (i.e., those with
465 conductivity ranging between of 5 and 150 mS/cm), and ultimately halite crystallization to drive
466 Li concentration (in the brine) to the highest levels (Munk et al., 2018). Moreover, recent studies
467 reported that Li content and isotopic composition in the Cenozoic volcanic rocks of the Central
468 Andes can be explained by assimilation of the Paleozoic basement, and that volcanic and
469 Paleozoic basement rocks are considered to be the primary source of Li in the Andean plateau
470 (García et al., 2019; Meixner et al., 2019). These elements may help understanding the lack of
471 spatial pattern in the regional Li distribution. The fact that Li is sourced from a lithologic
472 sequence that is widespread across the entire Puna would rule out a geographic control. Rather,
473 consistently increasing Li grades with salar size define a pattern that depends on basin scale
474 processes, on geomorphology and, perhaps, also on the age of the basin (i.e., older basins would
475 have more time than younger ones to stock the products of weathering and evaporation).

476

477 *5.3. The Li-bearing Southern Puna salars in an Andean context*

478 It is commonly assumed that brines enriched in Li also have high concentrations of K
479 and B. In Li brine-type deposits, K is typically obtained during Li recovering processes via
480 brine evaporation, and borate mines are widespread in Andean salars. Positive trends between
481 Li^+ - K^+ and Li^+ - B have been observed in CE, IN, PZ, AN, and PC (Fig. 6). Similar patterns
482 have been also reported in salars of the Northern Puna. Furthermore, positive correlations might
483 also exist between Li^+ - Mg^{2+} and K^+ - Mg^{2+} in CE, AN, RI, RG, and the Northern Puna's salars

484 of Olaroz, Cauchari, Salinas Grandes, and Jama. These features could suggest common sources
485 and a similar geochemical behavior for these ions.

486 Boron isotopic studies reported in the literature for the Puna region suggest the existence
487 of two distinctive sources of B, one associated with volcanic activity controlling borate
488 precipitation in western Puna salars, and another one related to weathering of basement rocks,
489 prevailing in the eastern Puna (Kasemann et al., 2004). Accordingly, given the better correlation
490 between Li^+ and B in the eastern Puna salars, we suggest that some of their Li^+ and B may have
491 been provided by weathering of the Ordovician basement. Furthermore, Peralta Arnold et al.
492 (2017) reported isotopic data ($\delta^{18}\text{O}$ and δD) coupled with high lithium concentrations in mature
493 thermal waters (between 4 to 80 mg L^{-1}) and in waters recycling evaporites (up to 600 mg L^{-1}),
494 which revealed that rock weathering is likely a significant supplying process for these salars.

495 A comparison between the concentrations of TDS-normalized ions (Figs. 8 and 11)
496 allows assessing the relative abundance of Li^+ and other ions with respect to salinity (i.e., brine
497 evolution and concentration through evaporation). Our data reveal that, relatively to those of
498 their respective neighboring salars, brines from HM, DI, AR and IN are proportionally richer
499 in K^+ (Fig. 11D), those from AR and AN are richer in B (Fig. 11 F), and the CE, PG, and HM
500 brines are the richest in Li^+ (Figs. 8 B, and 11). IN and, to a lesser extent, AR and DI, also
501 contain the highest TDS-normalized Mg^{2+} grades in the Southern Puna (Fig. 11). The Salar de
502 Arizaro, the largest salar of the Argentine Puna, has a mean $\text{Li}^+:\text{Mg}^{2+}$ of only 0.16, similar to
503 that of Atacama in Chile (Fig. 12, Table 2). It is important to note that reference values of the
504 mean $\text{Li}^+:\text{Mg}^{2+}$ ratio in operating Li brine-type mines of the Andean plateau are highly variable:
505 0.16 in Atacama, 0.89 in Olaroz, and ~ 0.90 in Hombre Muerto (Ericksen and Salas, 1977;
506 Risacher and Fritz, 1991; Godfrey et al., 2013; López Steinmetz et al., 2018; see Fig. 12 and
507 $\text{Li}^+:\text{Mg}^{2+}$ ratios summarized in Table 2). Therefore, in operative terms, there is no strict
508 threshold values to be considered as an acceptable $\text{Li}^+:\text{Mg}^{2+}$ ratio. Quite the reverse, Li grades

509 define the major criteria to operate a brine-type project (Fig. 12). Additionally, and subsidiary
510 to Li grades, the attractiveness of a Li brine-type mining project will also be reliant on the
511 $\text{Li}^+:\text{Mg}^{2+}$ ratios and salar size and shape, as larger and more near-circular salt pans are better
512 able to support long-term extraction than smaller ones or those having elongated shapes
513 (Houston et al., 2011). Moreover, the resource estimate of a salt pan considers the aquifer
514 geometry and the area of the concession, as deposits having a higher storage (i.e., the scale of
515 the recoverable reserve of brine) provide, in general, more economic interest than smaller ones
516 to develop Li brine-type mining (Gruber et al., 2010; López Steinmetz and Fong, 2019).

517 The Southern Puna remains a very remote and difficult to access region, due to poor
518 roads conditions. Because of this, the location of salars in the Southern Puna is a constraint for
519 operations compared with those located in the northern part, where roads and distances are
520 suitable. Nevertheless, comparing Li grades, mean $\text{Li}^+:\text{Mg}^{2+}$ ratios, and salar sizes can provide
521 a rapid evaluation of the relative mining potential of these salars with respect to Li extraction
522 (Fig. 12). Applying these considerations to the salars that are not being operated, the most
523 interesting targets in Southern Puna are the Salar de Arizaro (the largest salt pan of the
524 Argentine Puna), Antofalla-Botijuelas (which has interesting Li:Mg ratios and a large surface,
525 though its elongated shape could be a constraint), and Pastos Grandes, Pozuelos, and Rincón
526 (which have encouraging Li grades, interesting sizes, and relatively easy access). These salars
527 embody interesting perspectives in a regional context.

528

529

6. Conclusions

530 This study reports the results of a regional geochemical survey of Li brines, covering
531 the Southern Puna of Argentina. Brines from the twelve major salars in this region are
532 characterized by mean Li^+ concentrations varying by up to one order of magnitude, from 57 to
533 570 mg L^{-1} , with mean Li:Mg ratios ranging from 0.01 to 1.24.

534 Brines are of the $\text{Na}^+ / \text{Cl}^- - \text{SO}_4^{2-}$ type and are relatively rich in K^+ and Mg^{2+} . Data
535 presented in this contribution reveal likely correlations between the concentrations of Li^+ , K^+ ,
536 B, and Mg^{2+} , suggesting common sources and similar geochemical behavior for these ions. No
537 geographical pattern for the Li^+ concentrations has been observed. However, salar size could
538 be related to maximum Li^+ grade of brines. Larger salars would then be expected to contain
539 higher Li^+ grade brines than smaller ones, making salar size a useful criterion for surveying
540 brine-type deposits.

541 The comparison between mean Li^+ grades, $\text{Li}^+:\text{Mg}^{2+}$ ratios, and salar size provides an
542 assessment of the Li potential offered by a number of salars in the Souther Puna: Arizaro
543 because of it dimension, Pastos Grandes, Pozuelos, and Rincón due to Li grades and
544 accessibility, and Antofalla-Botijuelas on account of its Li:Mg ratios. In addition to these salars,
545 Río Grande and Salinas Grandes have a remarkable brine chemistry. Olaroz, Cauchari, and
546 Hombre Muerto contain the highest Li^+ grades in brines of all of the Argentine Puna, and
547 represent the most interesting perspectives of the Argentine plateau and in a regional context.

548

549

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References

557 Aceñolaza, F., 1973, El Ordovícico de la Puna saltocatarqueña: 5th Congreso Geológico
558 Argentino, Actas v. 4, p. 3-18.

559 Aceñolaza, F.; Benedetto, L.; Salfity, J., 1972, El Neopaleozoico de la Puna: su fauna y
560 correlación con áreas vecinas: *Anales de la Academia Brasileira de Ciencias*, v. 44, p. 5-
561 20.

562 Alonso, R.N., 1986, Ocurrencia, Posición Estratigráfica y Génesis de los Depósitos de Boratos
563 de la Puna Argentina: Unpublished PhD Thesis, Universidad Nacional de Salta, 196 pp.

564 Alonso, R.N.; Gutiérrez, R.; Viramonte, J., 1984, Puna Austral - Bases para el
565 subprovincialismo geológico de la Puna Argentina: 9th Congreso Geológico Argentino,
566 *Actas v. 1*, p. 43-63.

567 Alonso, R.N.; Viramonte, J.G., 1987, Geología y metalogenia de la Puna: *Estudios Geológicos*,
568 v. 43, p. 393-407.

569 Alonso, R.N.; Jordan, T.E.; Tabbutt, K.T.; Vandervoordt, D.S., 1991, Giant evaporite belts of
570 the Neogene central Andes: *Geology*, v. 19 (4), p. 401-404.

571 Bahlburg, H.; Berndt, J.; Gerdes, A.; 2016, The ages and tectonic setting of the Faja Eruptiva
572 de la Puna oriental, Ordovician, NW Argentina: *Lithos*, v. 256-257, p. 41-54.

573 Barcelos Haag, M.; Beaz, W.; Sommer, C.A.; Arnosio, J.M.; Filipovich, R.E., 2019,
574 Geomorphology and spatial distribution of monogenic volcanoes in the southern Puna
575 plateau (NW Argentina): *Geomorphology*, v. 342, p. 196-209.

576 Buatois, L.A.; Mángaro, M.G., 2003, Sedimentary facies, depositional evolution of the Upper
577 Cambrian–Lower Ordovician Santa Rosita formation in northwest Argentina: *Journal*
578 *of South American Earth Sciences*, v. 16, p. 343-363.

579 Caffè, P.J.; Trumbull, R.B.; Coira, B.L.; Romer, R.L., 2002, Petrogénesis of Early Neogene
580 magmatism in the Northern Puna; implications for magma genesis and crustal processes
581 in the Central Andean Plateau: *Journal of Petrology*, v. 43, p. 907-942.

582 Clesceri, L.S.; Greenberg, A.E.; Eaton, A.D., 1998, *Standard Methods for the Examination of*
583 *Water and Waste Water: Amer. Public. Health. Assoc., 20th Edition, USA.*

584 Coira, B., 1979, Descripción geológica de la Hoja 3c: Servicio Geológico Nacional. Buenos
585 Aires, Boletín 170.

586 de Silva, S.L., 1989, Altiplano–Puna volcanic complex of the central Andes: *Geology*, v. 17, p.
587 1102-1106.

588 Donato, E.; Vergani, G., 1985, Geología del Devónico y Neopaleozoico de la zona del Cerro
589 Rincón, Salta, Argentina: 4th Congreso Geológico Chileno, Actas v. 1 (1), p. 262-283.

590 Egenhoff, S.O.; Lucassen, F., 2003, Chemical and isotopic composition of lower to upper
591 Ordovician sedimentary rocks (Central Andes /South Bolivia): implications for their
592 source: *Journal of Geology*, v. 111, p. 487-497.

593 Ericksen, G.E.; Salas, R., 1977, Geology and resources of salars in the central Andes: U.S.
594 Geological Survey, Open File Repository 88-210, 51 pp.

595 Galli, C.I.; Moya, M.C.; Arnosio, M., 2010, Estudios sedimentológicos en los depósitos
596 carboníferos y pérmicos del borde occidental de la Puna: *Revista de la Asociación*
597 *Geológica Argentina*, v. 66, p. 119-132.

598 García, M.G.; Borda, L.G.; Godfrey, L.V.; López Steinmetz, R.L.; Losada Calderón, A., 2019,
599 Characterization of lithium cycling in the Salar de Olaroz, Central Andes, using a
600 geochemical and isotopic approach: *Chemical Geology*, v. 531, 119340,
601 <https://doi.org/10.1016/j.chemgeo.2019.119340>.

602 Garrett, D.E., 2004, Handbook of lithium and natural calcium chloride: their deposits,
603 processing, uses and properties: Elsevier Academic Press, 1st edition.

604 Ghadbeigi, L.; Harada, J.K.; Lettiere, B.R.; Sparks, T.D., 2015, Performance and resource
605 considerations of Li-ion battery electrode materials: *Energ. Environ. Sci.*, v. 8, p. 1640-
606 1650.

607 Godfrey, L.V.; Chan, L.-H.; Alonso, R.N.; Lowenstein, T.K.; McDonough, W.F.; Houston, J.;
608 Li, J.; Bobst, A.; Jordan, T.E., 2013, The role of climate in the accumulation of lithium-
609 rich brine in the Central Andes: *Applied Geochemistry*, v. 38, p. 92-102.

610 Grosse, P.; Guzmán S.; Petrinovic, I.A., 2017, Volcanes compuestos cenozoicos del noroeste
611 argentine: 20 Congreso Geológico Argentino, Relatorio, 484-517.

612 Grosse, P.; Orihashi, Y.; Guzmán, S.; Sumino, H.; Nagao, K., 2018, Eruptive history of
613 Incahuasi, Falso Azufre and El Cóndor Quaternary composite volcanoes, southern
614 Central Andes: *Bulletin of Volcanology*, v. 80, 44.

615 Gruber, P.W.; Medina, P.A.; Keoleian, G.A.; Kesler, S.E.; Everson, M.P.; Wallington, T.J.,
616 2010, Global lithium availability: a constraint for electric vehicles? : *Journal of*
617 *Industrial Ecology*, v. 15, p. 760-775.

618 Hache, E. ; Bonnet, C. ; Seck, G.S. ; Simoën, M., 2018, Les matériaux de la transition
619 énergétique : le lithium : The Conversation 24 October 2018
620 [https://theconversation.com/les-materiaux-de-la-transition-energetique-le-lithium-](https://theconversation.com/les-materiaux-de-la-transition-energetique-le-lithium-105429)
621 [105429](https://theconversation.com/les-materiaux-de-la-transition-energetique-le-lithium-105429).

622 Hardie, L.; Eugster, H., 1970, The evolution of closed-basin brines. Fiftieth Anniversary
623 Symposia, Mineralogy and Geochemistry of Non-Marine Evaporites: Mineralogical
624 Society of America Special Publication, p. 273-290.

625 Houston, J.; Butcher, A.; Ehren, P.; Evans, K.; Godfrey, L., 2011, The evaluation of brine
626 prospects and the requirement for modifications to filing standards: *Economic Geology*,
627 v. 106, p. 1225-1239.

628 Ide, F.; Kunasz, I.A., 1989, Origin of lithium in Salar de Atacama, northern Chile, in: Ericksen,
629 G.E., Cañas, M.T., Pinochet, J.A., Reinemund, R., eds., *Geology of the Andes and its*
630 *relation to hydrocarbon and mineral resources*, Circum-Pacific Council for Energy and
631 *Mineral Resources*, Earth Science Series, v. 11, p. 165-172.

632 Jordan, T.; Alonso, R.N., 1987, Cenozoic stratigraphy and basin tectonics of the Andes
633 Mountain: American Association of Petroleum Geologist, v. 71, p. 49-64.

634 Kaseman, S.A.; Meixner, A.; Erzinger, J.; Viramonte, J.G.; Alonso, R.N.; Franz, G., 2004,
635 Boron isotope composition of the geothermal fluids and borate minerals from salar
636 deposits (central Andes / NW Argentina): Journal of South American Earth Sciences, v.
637 16, p. 685-697.

638 Kesler, S.E.; Gruber, P.W.; Medina, P.A.; Keoleian, G.A.; Everson, M.P.; Wallington, T.J.,
639 2012, Global lithium resources: relative importance of pegmatites, brine and other
640 deposits: Ore Geology Reviews, v. 48, p. 55-69.

641 Kay, S.M.; Coira, B.L.; Caffè, P.J.; Chen, C.H., 2010, Regional chemical diversity, crustal and
642 mantle sources and evolution of central Andean Puna plateau ignimbrites: Journal of
643 Volcanology and Geothermal Research, v. 198, p. 81-111.

644 Kunasz, I.A., 2006, Lithium resources. In Industrial minerals and rocks, commodities, markets
645 and uses. 7th edition.

646 López Steinmetz, R.L., 2017, Lithium- and boron-bearing brines in the Central Andes:
647 exploring hydrofacies on the eastern Puna plateau between 23° and 23°30'S:
648 Mineralium Deposita, v. 52, p. 35-50.

649 López Steinmetz, R.L.; Galli, C.I., 2015, Hydrological change during the Pleistocene-Holocene
650 transition associated with the Last Glacial Maximum-Altithermal in the eastern border
651 of northern Puna: Andean Geology, v. 42 (1), p. 1-19.

652 López Steinmetz, R.L.; Salvi, S.; García, M.G.; Béziat, D.; Franco, G.; Constantini, O.;
653 Córdoba, F.; Caffè, P.J., 2018, Northern Puna plateau-scale survey of Li brine-type
654 deposits in the Andes of NW Argentina: Journal of Geochemical Exploration, v. 190, p.
655 26-38.

656 López Steinmetz, R.L.; Fong, S.B., 2019. Water legislation in the context of lithium mining in
657 Argentina: Resources Policy, v. 64, 101510.

658 Lucassen, F.; Becchio, R.; Franz, G., 2011, The early Palaeozoic high grade metamorphism at
659 the active continental margin of West Gondwana in the Andes (NWArgentina/N Chile):
660 International Journal of Earth Sciences (Geologische Rundschau), v. 100, p. 445-463.

661 Maro, G.; Caffè, P.J., 2013, Primer registro de lavas shoshoníticas en Puna norte, el cerro Barro
662 Negro: 2 Simposio sobre Petrología Ignea y Metalogénesis Asociada, San Luis, Actas,
663 51 pp.

664 Maro, G.; Caffè, P.J.; Báez, W., 2017a, Volcanismo monogenético máfico cenozoico de la
665 Puna: 20 Congreso Geológico Argentino, Relatorio, p. 584-577.

666 Maro, G.; Caffè, P.J.; Romer, R.L.; Trumbull, R.B., 2017b, Neogene mafic magmatism in the
667 Northern Puna plateau, Argentina: generation and evolution of a back-arc volcanic suite:
668 Journal of Petrology, v. 58, p. 1591-1618.

669 Meixner, A.; Sarchi, C.; Lucassen, F.; Becchio, R.; Caffè, P.J.; Lindsay, J.; Rosner, M.;
670 Kasemann, S.A., 2019, Lithium concentrations and isotope signatures of Palaeozoic
671 basement rocks and Cenozoic volcanic rocks from the Central Andean arc and back-arc:
672 Mineralium Deposita, doi: 10.1007/s00126-019-00915-2.

673 Méndez, V.; Navarini, A.; Plaza, D.; Viera, O., 1973, Faja Eruptiva de la Puna oriental: 5th
674 Congreso Geológico Argentino, Actas v. 4, p. 89-100.

675 Méndez, V.; Turner, J.C.; Navarin, A.; Amengual, R.; Viera, O., 1979, Geología de la región
676 Noroeste. Argentina: Dirección General de Fabricaciones Militares. Buenos Aires, 118
677 pp.

678 Moya, M.C., 1988, Lower Ordovician in the Southern part of the Argentine Eastern Cordillera,
679 in: Bahlburg, H., Breitkreuz, Ch., P. Giese, eds., The Southern Central Andes, Springer,
680 Berlin, p. 55-69.

681 Montero López, C.; Guzmán, S.; Barrios, F., 2015, Late Miocene ignimbrites at the southern
682 Puna- northern Sierras Pampeanas border (~27° S): stratigraphic correlation: Journal of
683 South America Earth Sciences, v. 62, p. 89-91.

684 Munk, L.A.; Hynek, S.A.; Bradley, D.; Boutt, D.; Labay, K.; Jochens, H., 2016, Lithium
685 brines: A Global Perspective: Reviews in Economic Geology, v. 18, p. 339-365.

686 Munk, L.A.; Boutt, D.F.; Hynek, S.A.; Moran, B.J., 2018, Hydrogeochemical fluxes and
687 processes contributing to the formation of lithium-enriched brines in a hyper-arid
688 continental basin: Chemical Geology, v. 493, p. 37-57.

689 Olivetti, E.A.; Ceder, G.; Gaustad, G.G.; Fu, X., 2017, Lithium-Ion Battery Supply Chain
690 Considerations: Analysis of Potential Bottlenecks in Critical Metals: Joule, v. 1, p. 229-
691 243.

692 Orberger, B.; Rojas, W.; Millot, R.; Flehoc, C., 2015, Stable isotopes (Li, O, H) combined with
693 chemistry: powerful tracers for Li origins in Salar deposits from the Puna region,
694 Argentina: Procedia Earth and Planetary Science, v. 13, p. 307-311.

695 Ovejero Toledo, A.; Alonso, R.N.; Ruiz, T.; Quiroga, A.G., 2009, Evapofacies halítica en el
696 Salar del Rincón, Departamento Los Andes, Salta: Revista de la Asociación Geológica
697 Argentina, v. 64 (3), p. 493-500.

698 Peralta Arnold, Y.J.; Cabassi, J.; Tassi, F.; Caffè, J.P.; Vaselli, O., 2017. Fluid geochemistry of
699 a deep-seated geothermal resource in the Puna plateau (Jujuy Province, Argentina):
700 Journal of Volcanology and Geothermal Research, doi:
701 10.1016/j.jvolgeores.2017.03.030.

702 Risacher, F.; Fritz, B., 1991, Quaternary geochemical evolution of the Salar of Uyuni and
703 Coipasa, Central Altiplano, Bolivia: Chemical Geology, v. 90, p. 211-231.

704 Risacher, F.; Fritz, B., 2009, Origin of salt and brine evolution of Bolivian and Chilean Salars:
705 Aquat. Geochemistry, v. 15, p. 123-157.

706 Salfity, J.; Gorustovich, S.; Moya, C.; Amengual, R., 1984, Marco tectónico de la
707 sedimentación y la efusividad cenozoicas en la Puna argentina: 9th Congreso Geológico
708 Argentino, Actas v. 1, p. 539-554.

709 Schnurr, W.B.W.; Trumbull, R.B.; Clavero, J.; Hahne, K.; Siebel, W; Gardeweg, M., 2007,
710 Twenty-five million years of silicic volcanism in the southern central volcanic zone of
711 the Andes: geochemistry and magma genesis of ignimbrites from 25 to 27S, 67 to 72W:
712 Journal of Volcanology and Geothermal Research, v. 166, p. 17-46.

713 Schwab, K., 1973, Die Stratigraphie in der umgebung des salar Cauchari : Geotekt. Forsch.,
714 v.43, 168 pp.

715 Sun, X.; Hau, H.; Zhao, F.; Liu, Z., 2017, Tracing global lithium flow: A trade-linked material
716 flow analysis: Resources, Conservation & Recycling, v. 124, p. 50-61.

717 Turner, J.C., 1960, Estratigrafía del Nevado de Cachi y sector oeste: Acta Geológica Lilloana,
718 v. 3, p. 191-226.

719 Turner, J.C. ; Méndez, V., 1979, Puna : Geología Regional Argentina, v. 1, p. 13-56. Buenos
720 Aires.

721 Vinante, D.; Alonso, R.N., 2006, Evapofacies del salar de Hombre Muerto, Puna argentina:
722 distribución y génesis: Revista de la Asociación Geológica Argentina, v. 61 (2), p. 286-
723 297.

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725

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Figure Captions

727

728 Fig.1. (A) Schematic map showing the location and geographic environment of the Puna plateau
729 in the Central Andes. The thick dashes separate the areas known as Altiplano, Northern and
730 Southern Puna (modified from López Steinmetz et al., 2018). (B) Location map zooming on

731 Argentinian Puna, showing the main salars in this region. Figure B is a subset of Figure A. 1:
732 Guayatayoc; 2: Salinas Grandes; 3: Olaroz; 4: Cauchari; 5: Jama; 6: Pastos Grandes; 7:
733 Pozuelos; 8: Centenario; 9: Ratones; 10: Diablillos; 11: Hombre Muerto; 12: Incahuasi; 13:
734 Antofalla-Botijuelas; 14: Río Grande; 15: Arizaro; 16: Pocitos-Quirón; 17: Rincón.

735

736 Fig. 2. (A) Schematic geological map of Southern Puna showing the location of eleven
737 considered salars (modified from Alonso and Viramonte, 1987). Insets display in detail the
738 location of shallow brine sampling sites (colored crosses) and corresponding Li grades (mg L^{-1})
739 of each salar located along the eastern border of the Southern Puna: Pastos Grandes (PG),
740 Pozuelos (PZ), Centenario (CE), Ratones (RA), Diablillos (DI), Hombre Muerto (HM), and
741 Incahuasi (IN). The western Southern Puna salars are: Antofalla-Botijuelas (AN), Río Grande
742 (RG), Pocitos-Quirón (PC), Rincón (RI), and Arizaro (AR). Precise latitude and longitude of
743 the samples are given in Table A1 of the Appendix. Lithological legend: 1) modern salar; 2)
744 lagoon; 3) muddy salt flat; 4) Quaternary alluvial deposits, including piedmonts, alluvial fans
745 and alluvial plains; 5) Quaternary basalt; 6) Neogene dacite, andesite, and ignimbrite; 7)
746 Cenozoic sedimentary units (Pastos Grandes Group); 8) upper Paleozoic sedimentary units
747 (Cerro Oscuro and Arizaro Formations); 9) Eastern Puna Eruptive Belt; 10) Ordovician
748 metasedimentary rocks (Copalayo, Caucota, and Falda Ciénaga Formations), including
749 ultramafic intrusions and inter-stratified volcanic rocks.

750

751 Fig. 3. Schematic maps displaying the location of shallow brine sampling sites (colored crosses)
752 and corresponding Li grades (mg L^{-1}) in salars located across the western Southern Puna:
753 Antofalla-Botijuelas (AN), Río Grande (RG), Pocitos-Quirón (PC), Rincón (RI), and Arizaro
754 (AR). The location of insets is provided in Figure 2A. Precise latitude and longitude of the

755 samples are given in Table A1 of the Appendix. Lithological legend as for Figure 2, plus 11)
756 thermal spring.

757

758 Fig. 4. Ternary diagrams displaying relative ionic concentrations (mg L^{-1}) measured in brines
759 from salars of the Southern Puna. A) Salars of the eastern area. B) Salars of the western part.
760 Salar abbreviations are Antofalla-Botijuelas (AN), Arizaro (AR), Centenario (CE), Ratones
761 (RA), Diablillos (DI), Hombre Muerto (HM), Incahuasi (IN), Pastos Grandes (PG), Pocitos-
762 Quirón (PC), Pozuelos (PZ), Rincón (RI), and Río Grande (RG).

763

764 Fig. 5. Scatter diagrams plotting the concentrations of Na^+ versus Cl^- (A), Ca^{2+} versus CO_3^{2-}
765 $+\text{HCO}_3^-$ (B), Ca^{2+} versus SO_4^{2-} (C), and Mg^{2+} versus SO_4^{2-} (D), in the twelve salars from the
766 Southern Puna. Abbreviations as in Fig. 4.

767

768 Fig. 6. Scatter diagrams showing the variation of the Li:K (A and B), the Li:B (C and D), and
769 the Li:Mg (E and F) ratios in salars from the Southern Puna. A, C, E) Salars of the western side.
770 B, D, F) Salars of the eastern part. Abbreviations as in Fig. 4.

771

772 Fig. 7. Schematic diagram of Hardie and Eugster (1970, modified after Risacher and Fritz,
773 2009) illustrating flow paths of the evaporative composition of inflow waters with respect to
774 salinity and composition, measured in the salars from Southern Puna. The ordinate axis plots
775 the total dissolved load of the solution in g L^{-1} . Abbreviations as in Fig. 4.

776

777 Fig. 8. Diagram showing the salinity grades (A) and the TDS normalized concentrations of Li^+
778 (B) of brines from Southern Puna salars. Abbreviations as in Fig. 4.

779

780 Fig. 9. Scatter diagrams showing the variations of Li^+ versus TDS (A), and Li^+ versus Na^+ (B)
781 in salars from the Southern Puna. Concentrations are expressed in mg L^{-1} . R is the Pearson
782 correlation coefficient. Abbreviations as in Fig. 4.

783

784 Fig. 10. Scatter diagrams showing the correlations between the maximum measured Li^+ grade
785 in brines and salar size, for the Puna plateau. R is the Pearson correlation coefficient. Li^+ -grade
786 brine data and salar size for JA, OL, CA, SG, and GG are from López Steinmetz et al. (2018)
787 and López Steinmetz (2017). Figure B is a subset of Figure A. Abbreviations as in Fig. 4, plus
788 Guayatayoc (GG), Salinas Grandes (SG), Olaroz (OL), Cauchari (CA), Jama (JA) from
789 Northern Puna (López Steinmetz et al., 2018).

790

791 Figure 11. Scatter diagrams showing the TDS-normalized concentrations of Li^+ versus Cl^- (A),
792 Li^+ versus Na^+ (B), Li^+ versus $\text{CO}_3^{2-} + \text{HCO}_3^-$ (C), Li^+ versus K^+ (D), Li^+ versus Mg^{2+} (E), and
793 Li^+ versus B (F) in salars of the Southern Puna. Abbreviations as in Fig. 4.

794

795 Figure 12. Scatter diagrams showing the variations of $\text{Li}^+:\text{Mg}^{2+}$ ratios versus salar size (A), and
796 the variations of mean Li^+ concentrations versus $\text{Li}^+:\text{Mg}^{2+}$ ratios (B). The middle panel is a
797 subset of Figure A. Abbreviations as in Fig. 10 plus Atacama (ATA) and Uyuni (UYU) from
798 Chile and Bolivia, respectively (data from Ericksen and Salas, 1977; Risacher and Fritz, 1991).
799 See Table 2 for data values. Note that regardless surfaces and Li:Mg ratios (A), only salars
800 having the highest Li grades are currently operated (B).

801

802

Table Captions

803

804 Table 1. Chemical composition of brines collected in salars of the Southern Puna: Antofalla-
805 Botijuelas (AN), Arizaro (AR), Centenario (CE), Diablillos (DI), Hombre Muerto (HM),
806 Incahuasi (IN), Pastos Grandes (PG), Pocitos-Quirón (PC), Pozuelos (PZ), Rincón (RI), and
807 Río Grande (RG).

808

809 Table 2. Comparative attributes of the Uyuni, Atacama, and the Argentine Puna's salars. The
810 mean Li^+ ^a concentration and the $\text{Li}:\text{Mg}$ ^a ratio in Uyuni corresponds to the mean values of 38
811 samples (from sample 100 to sample 133 and samples 146, 147 and 147A) reported by Ericksen
812 and Salas (1977). The mean Li^+ ^b concentration and $\text{Li}:\text{Mg}$ ^b ratio corresponds to mean values
813 of the 164 samples (from sample UA to sample RZ) reported by Risacher and Fritz (1991). The
814 mean Li^+ ^c concentration and $\text{Li}:\text{Mg}$ ^c ratio of Hombre Muerto correspond to the mean value of
815 the 9 samples (samples 4, 5, 6, and 9 to 14) reported by Godfrey et al. (2013). The mean Li^+ ^d
816 concentration in Hombre Muerto corresponds to the mean Li^+ concentration of 100 m-deep
817 brines reported by Garret (2004) and Kesler et al. (2012). The mean Li^+ ^e concentration
818 corresponds to the value reported by Ovejero Toledo et al. (2009) for brines at 10- to 50-m
819 depth in the Salar del Rincón. Data for Guayatayoc correspond to values reported by López
820 Steinmetz (2017), data for Jama, Olaroz, Cauchari, and Salinas Grandes are from López
821 Steinmetz et al. (2018). Remaining data is original from this contribution (Table 1).