

1 **The Origin of Continental Carbonates in Andean Salars:**  
2 **A Multi-Tracer Geochemical Approach in Laguna Pastos Grandes (Bolivia)**

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16 **Abstract**

17 In continental volcanic settings, abundant carbonate precipitation can occur with  
18 atypical facies compared to marine settings. The (bio-)chemical processes responsible for  
19 their development and early diagenesis are typically complex and not fully understood. In  
20 the Bolivian Altiplano, Laguna Pastos Grandes hosts a 40-km<sup>2</sup> carbonate platform with a  
21 great diversity of facies and provides an ideal natural laboratory to understand the processes  
22 responsible for the precipitation of carbonates in a continental province dominated by  
23 volcanism. In order to trace the origin of both water and solutes in the lagoon, the major  
24 element and stable isotope compositions ( $\delta^2\text{H}$ - $\delta^{18}\text{O}$ ,  $\delta^{37}\text{Cl}$ ,  $\delta^7\text{Li}$ ,  $\delta^{11}\text{B}$  and  $^{87}\text{Sr}/^{86}\text{Sr}$ ) of the  
25 spring and stream waters were characterized, as well as the stable isotope compositions  
26 ( $\delta^{13}\text{C}$ ,  $\delta^{15}\text{N}$ ) and noble gas isotope ratios of hydrothermal gases associated with spring  
27 waters. The results show that thermal springs discharging on the carbonate platform are  
28 close to saturation with calcite. PHREEQC modeling, together with fluid geochemistry and  
29 temperature estimated from a combination of geothermometers, indicate that Ca in these  
30 springs is inherited from the alteration of the volcanic bedrock by aqueous fluids heated at  
31  $\sim 225$  °C and enriched in magmatic mantle-derived CO<sub>2</sub>. Our results clearly show that the  
32 main driver for the precipitation of modern carbonates in Laguna Pastos Grandes is the  
33 deeply sourced CO<sub>2</sub>, which boosts the alteration of volcanic rocks at depth.

34  
35 **1. Introduction**

36 It has long been documented that continental carbonates can form, in varying abundances,  
37 both in pedogenetic profiles (see synthesis in Zamanian et al., 2016; Durand et al., 2018)  
38 and in palustrine-lacustrine environments (see synthesis in Alonso-Zarza and Tanner,  
39 2010; Verrecchia, 2007). Yet, their occurrences in continental volcanic provinces, typically

40 dominated by volcanoclastic, bio-silica, clay or evaporitic sediments, have not been  
41 investigated as much as their marine equivalents, generally considered as common  
42 hydrocarbon reservoirs and traditional archives of past oceans since the Archean. The  
43 recent discovery of hydrocarbon plays in Lower Cretaceous continental carbonates off the  
44 Brazilian coast changed this paradigm (Terra et al., 2010; Tosca and Wright, 2015) and  
45 promoted several studies focused on the origin and occurrence of carbonates in continental  
46 settings where the catchment and underlying rocks are mainly volcanic (e.g., Teboul et al.,  
47 2016; 2017).

48 Laguna Pastos Grandes in southern Bolivia includes a ~40 km<sup>2</sup> carbonate platform making  
49 it unique among the more than 200 salars scattered across the volcanic Central Andes  
50 region (Fig. 1a, b). Laguna Negra in Argentina is the only other Andean salar recently  
51 described with a significant, but much smaller (6.5 km<sup>2</sup>; Gomez et al., 2014), carbonate  
52 platform. Laguna Pastos Grandes exhibits a great diversity of calcitic, siliceous and  
53 evaporitic fabrics deposited in palustrine to shallow lacustrine environments, including  
54 some of the largest modern pisoliths discovered to date (Fig. 1c; Risacher and Eugster,  
55 1979; Jones and Renaut, 1994; Bougeault et al., 2019). In some ways, it may be considered  
56 as a modern equivalent of carbonate facies and processes that occurred during  
57 sedimentation of the Presalt facies in the volcanic-rich South Atlantic realm during the  
58 Early Cretaceous.

59 Although several studies were conducted on the hydrology and origin of chemical  
60 sediments in Bolivian and Chilean salars, a clear explanation for the abundance of modern  
61 carbonates in Laguna Pastos Grandes is still lacking. From structural, climatic and  
62 lithological points of view, Laguna Pastos Grandes seems to be similar to salars where  
63 carbonate precipitation is insignificant (Risacher et al., 2003; Risacher and Fritz, 2009; see  
64 geological setting). Indeed, while climatic parameters fundamentally control the existence  
65 and morphology of salars (Risacher and Fritz, 2009), the chemical composition of the  
66 brines and the nature of the precipitates in these lakes mainly depend on the initial  
67 composition of the inflow waters. In the present study, we thus performed a comprehensive  
68 geochemical study of gases and waters discharging on the carbonate platform of Laguna  
69 Pastos Grandes and of the brine filling the main basin.

70 The overarching goal of our research is to better understand the ongoing processes that  
71 allow for the rapid growth of these continental carbonates in a volcanic area under  
72 structural extension and fed by hydrothermal fluids. As a first step, this study focuses on  
73 the origin of the fluids and solutes from which carbonates have formed in the laguna based  
74 on the study of: (i) the chemical compositions of water samples from streams of the  
75 drainage area and hydrothermal springs upwelling through or near the carbonate platform  
76 and gas associated with the hydrothermal springs; (ii) the isotopic compositions of gas  
77 components ( $\delta^{13}\text{C}$ ,  $\delta^{15}\text{N}$  and noble gases), water samples ( $\delta^2\text{H}$  and  $\delta^{18}\text{O}$ ) and some of their  
78 solutes ( $\delta^{37}\text{Cl}$ ,  $\delta^7\text{Li}$ ,  $\delta^{11}\text{B}$  and  $^{87}\text{Sr}/^{86}\text{Sr}$ ); and (iii) Li, B and Sr isotopic compositions of  
79 volcanic rock samples surrounding the salar. These results, together with the temperature  
80 of the underlying geothermal reservoir estimated from a combination of geothermometers  
81 and with PHREEQC modeling of the hydrological system allowed us to identify the main

82 factor responsible for the abundant precipitation of modern carbonates in Laguna Pastos  
83 Grandes.

## 84 **2. Geological Setting**

85 Laguna Pastos Grandes is located in the southern part of the Bolivian Altiplano, in the  
86 South Lipez region. The Altiplano (3700 – 4500 m) is a major Plio-Pleistocene continental  
87 plateau bounded by the Eastern and Western Cordilleras and dominated by Cenozoic  
88 stratovolcanoes and their products (Fig. 1). To the south, rhyolitic ignimbrites and dacites  
89 to rhyodacites of the Altiplano-Puna Volcanic Complex (APVC) dominate the South Lipez  
90 region, whereas andesites to dacites predominate on the Chilean side (Thorpe et al., 1976).  
91 Native sulfur deposits occur on many volcanoes in Chile, and thermal springs are abundant.  
92 A thick succession of Cretaceous and Tertiary continental sediments, including evaporite  
93 deposits, outcrops in the Bolivian Eastern Cordillera and could be covered by volcanic  
94 rocks towards the west in the studied area (Deconinck et al., 2000).

95  
96 There are more than 200 closed basin lakes in the Bolivian Altiplano and Chilean Western  
97 Cordillera (Luddington et al., 1992). Most are saline and encompass a wide range of  
98 perennial or ephemeral lakes, locally termed “salars”. The two largest salars, Uyuni and  
99 Coipasa, are remnants of larger Pleistocene lakes and occupy the lower part of the Altiplano  
100 (3650 m altitude), whereas an abundance of smaller evaporitic basins (<400 km<sup>2</sup>) occur at  
101 higher altitudes (4000–4500 m) of the southern Altiplano (Fig. 1). The presence of these  
102 southern basins and their morphology primarily result from the cold and dry climate of this  
103 region, characterized by mean annual precipitations between 100 and 200 mm, air  
104 temperatures varying from -30 °C in winter to 25 °C in summer with daytime fluctuations  
105 of up to 40 °C, and annual evaporation of about 1400 mm (Risacher and Fritz, 1991).  
106 Although they belong to relatively similar environments in terms of geology and climate,  
107 Andean salars show a wide variety of brine compositions, which can be organized into  
108 three major groups: alkaline, sulfate-rich, and calcium-rich brines (Risacher and Fritz,  
109 2009). Different precipitates can be found in association with these brines, the most  
110 common being sodium chloride, sodium sulfates to borates, sodium carbonates and calcium  
111 sulfates (Risacher and Fritz, 2009). Their formation and evolution are thought to result  
112 from the combination of two fundamental factors: the presence of interior drainage basins  
113 as a source of solutes and high evaporation rates allowing salt precipitation (Risacher et  
114 al., 2003). Inflows to the Andean salars stem from various sources such as permanent and  
115 ephemeral streams, shoreline springs, groundwater discharge, and thermal springs. Most  
116 of the rainwater falling on the drainage area infiltrates and recharges underlying aquifers.  
117 Shoreline spring and hot-spring waters are typically enriched in solutes compared with  
118 streams due to the dissolution of ancient and/or present-day evaporitic sediments or  
119 through the infiltration and recycling of lake brines. Therefore, the composition of inflow  
120 waters feeding Andean salars reflects a mixture from two main sources: (1) dilute waters  
121 produced by the alteration of volcanic rocks by meteoric waters and (2) highly concentrated  
122 brackish waters derived from brine/salt recycling (Risacher et al., 2003 and references  
123 therein). The high rate of evaporation of these inflow waters in ponds and lakes increases  
124 the concentration of solutes and leads to the precipitation of a sequence of minerals in the  
125 order of their increasing solubility, following diverse evaporative pathways depending on  
126 the initial chemistry of inflow waters (Risacher and Fritz, 2009).

127

128 With an area of ~120 km<sup>2</sup>, Laguna Pastos Grandes is one of the largest salars of the  
129 southern Altiplano (Risacher and Eugster, 1979). This salar lies at an altitude of 4450 m in  
130 a 50-km-long caldera dated at 2.89±0.01 Ma by <sup>40</sup>Ar/<sup>39</sup>Ar of sanidine (Salisbury et al.,  
131 2011) and is probably the remnant of a larger lake that once occupied the caldera moat (de  
132 Silva and Francis, 1991). The drainage basin (660 km<sup>2</sup>) is limited to the west by rhyolitic  
133 lava ridges up to an elevation of 5800 m, and to the east by rhyolitic ignimbrite ridges up  
134 to an elevation of 5000 m (Fig. 1b). Coalescent alluvial fans with thin pebbly soils and  
135 xerophytic vegetation surround the laguna. Laguna Pastos Grandes can be divided into two  
136 main domains previously identified by Ballivian and Risacher (1981) and Jones and Renaut  
137 (1994): the eastern domain corresponds to a playa environment characterized by gypsum  
138 and carbonate muds associated with ulexite (NaCaB<sub>5</sub>O<sub>6</sub>(OH)<sub>6</sub>), and the western domain  
139 corresponds to a vast 40-km<sup>2</sup> palustrine carbonate platform, highly fragmented through  
140 cryoturbation exposing underlying recent carbonates (muds to calcarenites). Over these  
141 recent carbonate deposits, a few ponds no more than one decimeter deep host pisoliths and  
142 carbonate concretions up to 20 cm thick (Fig. 1c). Hydrothermal spring discharge over this  
143 platform produces important modern carbonate deposits (Bougeault et al., 2019).

### 144 3. Materials and Methods

#### 145 3.1 Water, gas and rock sampling

146 Nine water samples were collected during two sampling trips in January 2016 and  
147 March 2017, dry and wet seasons respectively (Tables 1, 2). We thus consider our samples  
148 as representative of the two main climatic seasons in terms of rainfall. Seven samples of  
149 water were selected from five thermal springs including one on the border of the laguna,  
150 two samples from cold streams, and one sample of brine from the southwestern part of the  
151 laguna (Fig. 2, Tables 1, 2). Two samples of fresh snow and one sample of rainfall were  
152 also collected respectively in January 2016 and March 2017 in order to constrain the  
153 meteoric sources of water in the area (Table A2).

154 Water samples were filtered using a 0.1 µm sterile acrylic filter (Sartorius Minisart®) fixed  
155 at the end of a 50 mL syringe. For cation analyses, ~20 ml samples were acidified with 3  
156 drops of HNO<sub>3</sub> (16N) in the field. The temperature and pH were measured on site at each  
157 collection point. In 2016, in the field, the total alkalinity was determined by H<sub>2</sub>SO<sub>4</sub> (1.6 N)  
158 titration using a manual titrator and adapted cartridge (Hach®; error below 1%, Table 2;  
159 Gran, 1952). Samples of 25 ml were titrated and 25 titrations (pH and volume of added  
160 titrated acid) were numerically processed using the Gran function (Gran, 1952). The  
161 correlation factors obtained by regression on the derivate of the titration curve are better  
162 than 0.998. In 2017, the total alkalinity was determined by end-point titration with HCl  
163 (1N or 0.1N) with an automatic titrimeter (Metrohm) at the Total laboratory (France, error  
164 below 1%; Rounds and Wilde, 2012). The bicarbonates alkalinity was calculated from the  
165 total alkalinity corrected from the contribution of weak acid and B(OH)<sub>4</sub><sup>-</sup> concentration.  
166 The B(OH)<sub>4</sub><sup>-</sup> concentration was calculated from the B concentration (obtained with ICP-  
167 AES) and the pH of the sampled solution. The weak acid (HCOO<sup>-</sup>; CH<sub>3</sub>COO<sup>-</sup>; C<sub>2</sub>H<sub>5</sub>COO<sup>-</sup>  
168 ; i-C<sub>3</sub>H<sub>7</sub>COO<sup>-</sup>; n-C<sub>3</sub>H<sub>7</sub>COO<sup>-</sup>) were measured by ionic chromatography (930 Compact IC  
169 Flex, Metrohm). Considering the high alkalinities of the samples, the contribution of OH<sup>-</sup>  
170 remains negligible. In this article, the alkalinity refers to the HCO<sub>3</sub><sup>-</sup>/CO<sub>3</sub><sup>2-</sup> alkalinity.

171  
172 Four thermal springs named *La Salsa*, *La Rumba*, *El Ojo Verde* and *El Gigante*  
173 (Fig. 2) were selected for both water and gas sampling on the carbonate platform based on

174 accessibility and high water-gas flux. *La Salsa*, *La Rumba* and *El Ojo Verde* springs contain  
175 bubbling sources of gas in water ponds whereas *El Gigante* is a dry source of gas (a mofet)  
176 away from the main water source. Gases were collected in March 2017 in 100- and 250-  
177 mL stainless-steel reservoirs and in four 12 mL Exetainer<sup>®</sup> vials, all previously evacuated  
178 to primary vacuum. To capture bubbling thermal spring gases, an inverted funnel  
179 connected to a rubber pipe was submerged in spring water and placed on top of the rising  
180 bubbles (Fig. A1). The other end of the pipe was connected through a T-junction to a  
181 stainless-steel fitting ending in a septum (for sampling in an Exetainer<sup>®</sup>) and a stainless-  
182 steel reservoir (for direct sampling) connected to a GA5000 gas detector (Scientific  
183 Instruments). Before collecting the gases accumulated in the funnel, the sampling system  
184 was completely flushed by the continuously outgassing bubbles to avoid air contamination  
185 (O<sub>2</sub> level typically below 2.0%).

186 Five rock samples of volcanic bedrock (2 andesites, 2 dacites and 1 ignimbrite of  
187 rhyolitic composition) were also collected on the border of the laguna (see location in Fig.  
188 2).

### 189 3.2 Analytical methods – Chemical compositions

#### 190 Gas composition

191 The gas composition was determined on the four samples collected in Exetainer<sup>®</sup> vials with  
192 a Varian 3800 high-resolution gas chromatograph (GC) equipped with Molsieve and  
193 Haesep type chromatographic columns at the IFPEN laboratory (Rueil-Malmaison,  
194 France). H<sub>2</sub> and He quantification was performed using a thermal conductivity detector  
195 (TCD) with N<sub>2</sub> as the carrier gas, whereas CO<sub>2</sub>, N<sub>2</sub>, O<sub>2</sub> and CH<sub>4</sub> were quantified using a  
196 TCD with He as the carrier gas. Relative concentrations were calculated after the  
197 chromatographic response had been calibrated in partial pressure for each compound using  
198 "Air Liquide TM" and "Saphir". These standards are quality gas mixtures that include H<sub>2</sub>,  
199 He, N<sub>2</sub>, CO<sub>2</sub>, O<sub>2</sub>, CH<sub>4</sub>, C<sub>2</sub>H<sub>6</sub>, C<sub>3</sub>H<sub>8</sub>, n-C<sub>4</sub>H<sub>10</sub> and i-C<sub>4</sub>H<sub>10</sub>, available in the laboratory at  
200 different concentrations bracketing the samples' composition range. Each sample analysis  
201 was followed by a blank analysis to ensure the absence of carry over. Results are given  
202 with a precision of ± 5 vol.% for O<sub>2</sub>, ±1.3 vol.% for CO<sub>2</sub>, ±3 vol.% for N<sub>2</sub> and ±0.1 vol.%  
203 for CH<sub>4</sub> based on replicate measurements of gas standards of similar concentrations.  
204

#### 205 Water composition

206 All chemical analyses were carried out in the Total laboratories (Pau, CSTJF, France) using  
207 ion chromatography (Cl, Br and SO<sub>4</sub>), Inductively Coupled Plasma-Atomic Emission  
208 Spectroscopy (Li, B and Sr), Inductively Coupled Plasma-Mass Spectrometry (Ca and  
209 Mg), and Flame Emission Spectrometry (Na, K, Ca and SiO<sub>2</sub>). Accuracy for major  
210 elements was better than ± 5% and verified by repeated measurements of certified standard  
211 materials, namely Ion96-3 and LGC6020 (river waters) for cations and anions, and diluted  
212 Li and B ICP-AES standard solutions (Merck). Saline samples were analyzed either after  
213 dilution (to minimize matrix effects during measurement) or by adding a standard (to match  
214 the matrix of the standard materials). The matrix effects were validated on at least three  
215 dilutions (500, 1000, 2000).

### 216 3.3 Analytical methods – Isotopic compositions

#### 217 CO<sub>2</sub> gas

218 The isotopic composition of the CO<sub>2</sub> gas was measured in Exetainer<sup>®</sup> vials at the IFPEN  
219 laboratory using a MAT253 (Finnigan Mat-Thermo Fisher) triple collection mass

220 spectrometer coupled to a gas chromatograph, operating with He as a carrier gas. An  
221 internal reference CO<sub>2</sub> gas was calibrated with the international gas reference standards  
222 RM8562, RM8563 and RM8564 with  $\delta^{13}\text{C}_{\text{VPDB}}$  of  $-3.76 \pm 0.03 \text{ ‰}$ ,  $-41.56 \pm 0.04 \text{ ‰}$  and  $-$   
223  $10.45 \pm 0.03 \text{ ‰}$ , respectively (Verkouteren and Klinedinst, 2004). All the isotopic  
224 compositions given in this study are reported in the usual  $\delta$ -scale in ‰ according to  $\delta_{\text{sample}}$   
225  $(\text{‰}) = \{(R_{\text{sample}}/R_{\text{standard}}) - 1\} \times 1000$ , where R is the  $^{13}\text{C}/^{12}\text{C}$  atomic ratio. The uncertainties  
226 on  $\delta^{13}\text{C}$  values are better than  $\pm 0.4 \text{ ‰}$  based on the external reproducibility of internal  
227 standards.

228

### 229 **N<sub>2</sub> gas**

230 The isotopic composition of N<sub>2</sub> in gas samples stored in Exetainer<sup>®</sup> vials or stainless-steel  
231 cylinders was measured at the Institut de physique du globe de Paris (IPGP, France). The  
232 N<sub>2</sub> was purified and isolated from other gases before being transferred to the IRMS dual-  
233 inlet mass spectrometer Delta + XP (Finnigan Mat-Thermo Fisher) for isotopic analyses.  
234 N<sub>2</sub> purification was performed using the high vacuum line ( $P < 10^{-5}$  mbar) described in Li  
235 et al. (2009) (details in Appendix). We obtained a relative uncertainty on the  $\delta^{15}\text{N}$  better  
236 than  $\pm 0.5 \text{ ‰}$  taking into account the N<sub>2</sub> extraction process efficiency and the  
237 reproducibility on an internal reference N<sub>2</sub> gas, itself calibrated against the air, the  
238 international reference standard for  $\delta^{15}\text{N}$  measurements.

239

### 240 **Noble gases**

241 Noble gas isotopic compositions were measured at IPGP using the Helix-SFT (Split Fight  
242 Tube, Thermo Instruments<sup>®</sup>) following the protocol of Moreira et al. (2018) (details in  
243 Appendix). For Ne and Ar, the standard is the atmosphere. The helium standard is a gas  
244 collected at the Irene thermal spring (Reunion island) with a  $^3\text{He}/^4\text{He}$  value (R) of  $12.56 \pm$   
245  $0.05 R_{\text{A}}$  (with  $R_{\text{A}}$  the  $^3\text{He}/^4\text{He}$  value of the air  $1.4 \times 10^{-6}$ ). For the present study, blank  
246 corrections were negligible. Final uncertainties for the isotopic ratios in samples are  $\pm 0.1$   
247 for  $R/R_{\text{A}}$ ,  $\pm 0.06$  for  $^{20}\text{Ne}/^{22}\text{Ne}$ ,  $\pm 0.0005$  for  $^{21}\text{Ne}/^{22}\text{Ne}$ ,  $\pm 5$  for  $^{40}\text{Ar}/^{36}\text{Ar}$  and correspond to  
248 the error propagation of the measured uncertainty, the blank correction, and the correction  
249 for mass discrimination.

250

### 251 **Water isotopes**

252 Oxygen and hydrogen isotope measurements were performed at BRGM stable isotope  
253 laboratory by equilibrating during one night 1 mL of water with gas mixtures of H<sub>2</sub>-He  
254 and CO<sub>2</sub>-He respectively for  $\delta^2\text{H}$  and  $\delta^{18}\text{O}$ , and using a Finnigan MAT 252 mass  
255 spectrometer (Assayag et al., 2008). The external precision was  $\pm 0.1 \text{ ‰}$  for  $\delta^{18}\text{O}$  and  $\pm$   
256  $0.8 \text{ ‰}$  for  $\delta^2\text{H}$  vs. SMOW.

257

### 258 **Chlorine**

259 The chlorine stable isotope compositions were measured at the IPGP on gaseous CH<sub>3</sub>Cl  
260 that was prepared and purified with the method described in Godon et al. (2004). The  $\delta^{37}\text{Cl}$   
261 measurements were then performed on the dual-inlet IRMS Delta + XP. They are reported  
262 in Table A4 with the conventional  $\delta^{37}\text{Cl}$  notation in per mil variations relative to Standard  
263 Mean Ocean Chlorine (SMOC). In this study, the external reproducibility of the seawater  
264 standard was  $0 \pm 0.04 \text{ ‰}$  (1s, n = 18) as routinely obtained at IPGP for more than two  
265 decades (Godon et al., 2004). Four pore fluid samples were measured twice. The mean  
266 difference between duplicates was  $0.04 \text{ ‰}$ .

267

268  **$\delta^7\text{Li}$  analysis**

269 In water samples, lithium isotopic compositions were measured using a Neptune  
270 Multi Collector ICP-MS (Thermo Fisher Scientific) at BRGM stable isotope laboratory.  
271  $^7\text{Li}/^6\text{Li}$  ratios were normalized to the L-SVEC standard solution (NIST SRM 8545)  
272 following the standard-sample bracketing method (Millot et al., 2004). The uncertainties  
273 on  $\delta^7\text{Li}$  values are better than  $\pm 0.5\%$  ( $2\sigma$ ) based on the external reproducibility using  
274 internal standards (seawater IRMM BCR-403 and basalt JB-2).

275 In volcanic rocks, Li was separated from the matrix by ion-exchange  
276 chromatography using the method described in detail by Dellinger et al. (2015). After  
277 digestion, a sample aliquot was loaded onto a column filled with AG50-X12 resin and the  
278 Li was eluted in HCl 0.2 N. The Li isotopic composition was measured by MC-ICP-MS  
279 Neptune (Thermo Scientific, Bremen) at IGP using an APEX desolvating system and at  
280 typical Li concentrations of 20–30 ppb. Each sample was successively measured three  
281 times within a standard-sample bracketing (SSB) sequence, yielding five  $\delta^7\text{Li}$  values from  
282 which an average value was derived. Data were corrected for the background intensities  
283 recorded before each bracketing standard and each sample. The intensity of the background  
284 was no more than 0.5–1% of the sample intensity. The overall reproducibility and accuracy  
285 of the procedure (including solid sample digestion and Li separation) was checked by  
286 measurement of the basalt reference material BHVO-2 ( $\delta^7\text{Li} = 4.23 \pm 0.83\%$ ; Ryu et al.,  
287 2014). The external error ( $2\sigma$ ) was better than 0.5%. Finally, the concentration of the total  
288 procedural blank (acid digestion and column chemistry) was assessed to be less than 0.05  
289 ng, i.e., insignificant compared with the amount of Li in the samples.

290  
291  **$\delta^{11}\text{B}$  analysis**

292 Boron isotopic compositions of water samples were determined on a Finnigan  
293 MAT 261 solid source mass spectrometer in a dynamic mode at BRGM stable isotope  
294 laboratory. For these samples, water volumes corresponding to a mass of 10  $\mu\text{g}$  of B  
295 underwent a two-step chemical purification using Amberlite IRA-743 selective resin  
296 according to a method adapted from Gaillardet and Allègre (1995). The uncertainties on  
297  $\delta^{11}\text{B}$  values are better than  $\pm 0.3\%$  ( $2\sigma$ ) based on the external reproducibility on the internal  
298 standard NBS951 ( $\delta^{11}\text{B} = 4.05398 \pm 0.00105\%$ ).

299 Rock samples were dissolved by alkali fusion and B was extracted following the  
300 procedure of Chetelat et al. (2009) (details in Appendix). Boron isotope ratios were  
301 determined by MC-ICP-MS with a direct injection nebulizer (d- DIHEN; Louvat et al.,  
302 2014a) at IGP with a  $2\sigma$  reproducibility between 0.05 and 0.3%.  $^{11}\text{B}/^{10}\text{B}$  values are  
303 expressed relative to the boric acid standard NBS 951 (NIST).

304  
305  **$^{87}\text{Sr}/^{86}\text{Sr}$  measurement**

306 For water samples, chemical purification of Sr ( $\sim 3 \mu\text{g}$ ) was performed using an ion-  
307 exchange column (Sr-Spec) before mass analysis according to a method adapted from Pin  
308 and Bassin (1992) with total blank  $< 1 \text{ ng}$  for the entire chemical procedure. After chemical  
309 separation, around 150 ng of Sr were loaded onto a tungsten filament with tantalum  
310 activator and analyzed with a Finnigan MAT 262 multi-collector mass spectrometer at  
311 BRGM's stable isotope laboratory. The  $^{87}\text{Sr}/^{86}\text{Sr}$  values were normalized to the certified  
312 value of the NBS987 standard 0.710240. An average internal precision of  $\pm 10 \text{ ppm}$  ( $2\sigma$ )  
313 was obtained and the reproducibility of the  $^{87}\text{Sr}/^{86}\text{Sr}$  ratio measurements was verified by  
314 repeated analysis of the NBS987 standard ( $^{87}\text{Sr}/^{86}\text{Sr} = 0.710243 \pm 10, 2\sigma$ ).

315 For volcanic rocks, after total evaporation of ~0.2 mL of rock sample digestion  
 316 solutions, the remaining solid was retaken with 0.1 mL of HNO<sub>3</sub> 3N and loaded onto a Sr-  
 317 SPEC (Eichrom) resin chromatography column to separate ca. 200 ng of Sr (Pin and  
 318 Bassin, 1992). The Sr isotopic composition was measured by MC-ICP-MS at IPGP. The  
 319 mass discrimination was corrected using the invariant ratio <sup>88</sup>Sr/<sup>86</sup>Sr (0.1194). Accuracy  
 320 and reproducibility were verified by repeated analysis of the NBS standard SRM 987  
 321 (<sup>87</sup>Sr/<sup>86</sup>Sr = 0.710250±0.0000025).

### 322 3.5 PHREEQC modeling

323 The PHREEQC software, version 3 (Parkhurst and Appelo, 2013) was applied to compute  
 324 aqueous speciation and fluid-mineral equilibria using the “thermoddem v1.10 06jun2017”  
 325 thermodynamic database (website <http://thermoddem.brgm.fr/>; Blanc et al., 2012).

## 326 4. Results

### 327 4.1 Gas molecular and noble gases composition

328 *Table 1. Analytical results of the gas sampled in 2017. δ<sup>15</sup>N and δ<sup>13</sup>C values are averaged*  
 329 *from multiple measurements (n=2-6) except for sample PG17\_116, which was analyzed*  
 330 *only once for δ<sup>15</sup>N (details in Table A1). See text for calculations of atmospheric N<sub>2</sub>*  
 331 *proportion, δ<sup>15</sup>N correction from atmospheric contribution and modeling results.*

Sample no.	PG17_100	PG17_112	PG17_116	PG17_117
Sample location	La Salsa	La Rumba	El Gigante	El Ojo Verde
Latitude (°S)	21.619349	21.638776	21.64819	21.651306
Longitude (°W)	67.848462	67.852883	67.848736	67.840695
Temperature (°C)	43.4	44.6	41.5	36.2
Major composition (vol.%)				
CO <sub>2</sub>	74.7	66.2	86.0	38.4
CH <sub>4</sub>	0.04	0.03	0.00	0.07
O <sub>2</sub>	3.36	2.01	1.63	4.76
N <sub>2</sub>	21.8	32.0	12.4	56.4
% N <sub>2</sub> atm	57.3	23.4	49.1	31.5
Isotopic composition (‰)				
δ <sup>13</sup> C (±0.1‰, 2σ)	-11.2	-11.2	-11.2	-11.0
δ <sup>15</sup> N (±0.5‰, 2σ)	2.7	1.8	1.6	2.3
δ <sup>15</sup> N <sub>primary</sub>	6.4	2.3	3.1	3.4
Noble gases (ppm)				
<sup>4</sup> He	337	517	109	814
<sup>20</sup> Ne	0.56	1.50	0.43	2.03
<sup>36</sup> Ar	7.1	12.9	3.6	12.2
<sup>40</sup> Ar/ <sup>36</sup> Ar	298	288	283	288
R <sub>C</sub> /R <sub>A</sub>	3.68	3.84	3.81	3.86
Mantle He (%)	45.4	47.3	47.1	47.6
CO <sub>2</sub> / <sup>3</sup> He <sub>surface</sub>	4.35*10 <sup>8</sup>	2.42*10 <sup>8</sup>	1.51*10 <sup>9</sup>	8.85*10 <sup>7</sup>
Modeling				
CO <sub>2</sub> / <sup>3</sup> He <sub>before degassing</sub>	1.2*10 <sup>8</sup>	9.6*10 <sup>8</sup>	2.9*10 <sup>9</sup>	4.7*10 <sup>8</sup>
CO <sub>2</sub> exsolution (%)	36	23	49	17

332



333 Thermal spring gases are mainly composed of CO<sub>2</sub> (38.4 to 86 vol. %) and N<sub>2</sub> (12.4 to 56.4  
 334 vol. %) with minor amounts of O<sub>2</sub> (1.63 to 4.76 vol. %) and negligible traces of CH<sub>4</sub> (<  
 335 0.07 vol. %; Table 1). No H<sub>2</sub> and H<sub>2</sub>S were detected. If we assume that O<sub>2</sub> is derived from  
 336 atmospheric contamination during sampling or natural diffusion into the thermal spring,  
 337 we obtain a contribution of associated atmospheric N<sub>2</sub> up to 57.3% of the total N<sub>2</sub> (Table  
 338 1). Abundances of the Atmosphere-Derived Noble Gases (ADNG: <sup>20</sup>Ne and <sup>36</sup>Ar) are  
 339 depleted relative to air and follow the composition expected for an Air Saturated Water  
 340 (ASW; Fig. 3). In contrast, <sup>4</sup>He is found in high proportions, from 109 to 814 ppm, with a  
 341 high <sup>3</sup>He/<sup>4</sup>He value normalized to air (R<sub>C</sub>/R<sub>A</sub>) of 3.79 ± 0.08 (with (<sup>3</sup>He/<sup>4</sup>He)<sub>air</sub> = 1.4x10<sup>-6</sup>;  
 342 Table 1). This value indicates a high mantle contribution (Sano and Marty, 1995, see  
 343 discussion).

#### 344 345 4.2 Gas C and N isotope compositions

346 The CO<sub>2</sub> gas sampled from thermal springs shows homogeneous δ<sup>13</sup>C values with an  
 347 average of -11.1 ± 0.1‰ (Table 1, A1). In contrast, the isotopic composition of N<sub>2</sub> (δ<sup>15</sup>N)  
 348 is more variable and ranges between 1.6 and 2.7 ± 0.5‰. Nitrogen isotope measurements  
 349 of sample PG17\_112 were performed on gases sampled in both Exetainers® and stainless-  
 350 steel tubes to ensure good reproducibility of the results, regardless of the container used  
 351 (Table A1). Similar values were obtained with a deviation of ±0.3‰. Considering an  
 352 atmospheric contamination of up to 57.3% for N<sub>2</sub>, we can estimate the primary δ<sup>15</sup>N value  
 353 by isotopic mass balance as follows:

$$354 \delta^{15}\text{N}_{\text{measured}} = \delta^{15}\text{N}_{\text{atm}} \cdot \%_{\text{atm}} + \delta^{15}\text{N}_{\text{primary}} \cdot (1 - \%_{\text{atm}})$$

355 With atmospheric contamination %<sub>atm</sub> up to 0.57 and δ<sup>15</sup>N<sub>atm</sub> = 0‰, a maximum δ<sup>15</sup>N<sub>primary</sub>  
 356 of 6.4‰ is obtained (Table 1). We thus consider the measured values as minimum values.  
 357

#### 358 359 4.3 Isotopic composition of water

360 361 *Table 2. Chemical and isotopic compositions of Laguna Pastos Grandes waters. NICB:*  
 362 *Normalized Ionic Charge Balance.*

Sample no.	PG17-117	PG17-112	PG17-100	PG1_1	MV_1	PGS_1	PG17_99	SP_3	LS_4
Sampling trip	2017	2017	2017	2016	2016	2016	2017	2016	2016
Name	El Ojo Verde spring	La Rumba spring	La Salsa spring	La Salsa spring	El Gigante spring	Piedmont spring	Stream	Stream	Lake brine
Lat. (°S)	21.651306	21.638776	21.619349	21.61934	21.64865	21.61996	21.60764	21.69665	21.69552
Lg. (°W)	67.840695	67.852883	67.848462	67.84842	67.84866	67.85628	67.75753	67.8098	67.80927
T (°C)	36.2	44.6	43.4	42.2	45.7	32.4	17.3	16.4	24.5
pH	6.41	5.99	6.90	6.42	6.20	6.35	9.15	7.99	7.39
Alkalinity on site				10.7	8.91	4.35		0.78	
Chemical composition (mM)									
Na	232	137	173	220	251	23.7	0.57	1.17	3924
K	12.9	8.7	12.5	13.4	16.6	1.8	0.14	0.36	131
Ca	10.9	6.5	10.1	11.4	12.8	0.7	0.17	0.37	59.7
Mg	5.8	2.8	5.2	5.4	6.0	0.4	0.13	0.18	54.6
Alkalinity	7.4	5.3	7.4	7.4	8.9	1.8	0.90	0.79	10.9
SO <sub>4</sub>	2.9	2.3	2.3	2.9	4.2	0.8	0.04	0.22	39.5
Cl	278	173	197	258	291	25.5	0.73	1.52	4375
Li	11.1	6.6	9.9	7.7	9.6	0.8	0.02	0.25	74.8
Sr	0.11	0.06	0.11	0.11	0.15	0.01	0.001	0.003	1.03
B	3.6	2.2	3.3	3.2	4.7	0.5	0.04	0.08	28.6

Br	0.073	0.046	0.069	0.060	0.070	0.006	0.006	0.006	0.426
SiO <sub>2</sub> *	116	101	116	155	152	101	36	60	60
Salinity**	16.2	10.1	11.5	15.1	17.0	1.49	0.04	0.09	256
NICB (%)	-1.3	-7.5	6.9	0.7	2.2	-3.1	-26.4	3.0	-2.9
pCO <sub>2</sub> (mbar)***	141	309	60.3	110.0	389.0	61.7	0.03	0.5	10.5
Isotopic compositions (‰ ±2s)									
δ <sup>2</sup> H (±0.8)	-92.2	-96.7	-93.9	-93.8	-92.5	-104.2	-99.4	-104.7	7.6
δ <sup>18</sup> O <sub>H<sub>2</sub>O</sub> (±0.1)	-11.4	-12.4	-11.8	-11.7	-11.4	-14.2	-13.1	-13.2	3.3
δ <sup>7</sup> Li	5.2 ±0.1	5.6 ±0.1	3.8 ±0.1	3.6 ±0.1	4.0 ±0.2	2.6 ±0.2	4.0 ±0.2	10.9 ±0.1	3.9 ±0.3
δ <sup>11</sup> B	-4.4 ±0.1	-5.0 ±0.1	-4.9 ±0.2	-4.3 ±0.3	-6.7 ±0.3	-6.0 ±0.3		0.0 ±0.3	-7.2 ±0.3
<sup>87</sup> Sr/ <sup>86</sup> Sr	0.708384	0.708412	0.708398	0.708396	0.708402	0.708354	0.707950	0.707646	0.708327
2 <sub>Sm</sub>	0.000005	0.000006	0.000010	0.000007	0.000006	0.000006	0.000010	0.000007	0.000007

363 \*mg/L; \*\*g/L; \*\*\*calculated with PHREEQC based on water chemistry

364

365 Spring waters exhibit a narrow range of δ<sup>18</sup>O (-14.2 to -11.4‰) and δ<sup>2</sup>H (-104.2 to -92.2‰),  
366 slightly more enriched in <sup>18</sup>O and <sup>2</sup>H than streams (with δ<sup>18</sup>O ~ -13.2‰ and -104.7 < δ<sup>2</sup>H  
367 < -99.4‰; Fig. 4, Table 2). They are located on the regional Ground and Spring Water Line  
368 (LGSWL; δ<sup>2</sup>H = 7.99 x δ<sup>18</sup>O + 0.3; n = 44) established by Fritz et al. (1981) and Rissmann  
369 et al. (2015) to the right of the Local Meteoric Water Line (LMWL) defined for modern  
370 precipitation in the Chilean and Bolivian Altiplano at altitudes of 2800 to 5700 m (δ<sup>2</sup>H =  
371 8.15 x δ<sup>18</sup>O + 15.3; Chaffaut et al., 1998). Streams and springs define a trend given by the  
372 following equation: δ<sup>2</sup>H = 4.29 x δ<sup>18</sup>O + 43.8 (R<sup>2</sup> = 95 %, n = 8; Fig. 4b) with δ<sup>18</sup>O and  
373 δ<sup>2</sup>H values more positive than rainfall collected at 4500 m during the wet season. Two  
374 snow samples collected during the dry season show more positive δ<sup>18</sup>O and δ<sup>2</sup>H values  
375 than rainfall and fall to the left of the LMWL trend (Table A2). The Piedmont thermal  
376 spring, located on the border of the laguna, is shifted from the other springs toward more  
377 negative δ<sup>18</sup>O and δ<sup>2</sup>H values. In the southeastern part of Laguna Pastos Grandes, the brine  
378 sampled from the lake (LS4 sample) is enriched in both <sup>18</sup>O and <sup>2</sup>H compared to the inlet  
379 waters and has even greater δ<sup>18</sup>O and δ<sup>2</sup>H values than other Andean salars (Fig. 4, Table  
380 A2).

381

382

#### 4.4 Geothermometry

383

384 The thermal waters associated with gases reach the surface at up to 46 °C, which is among  
385 the highest temperatures recorded in the Altiplano salars (Risacher and Fritz, 1991; Spiro  
386 et al., 1997). Based on the concentrations of some soluble elements (Si, Na, K, Ca, Mg, Li)  
387 in the thermal springs, we calculated the maximum temperature of the fluids at depth using  
388 empirical, semi-empirical and experimental equilibrium relations between water and  
389 minerals in the geothermal reservoirs (Sanjuan et al., 2014 and references therein). We  
390 used several geothermometers including silica, Na-K-Ca, Na-Li, Li-Mg, Li isotopes, and  
391 Na-K (details in Appendix; Table A3). They yield equilibrium temperatures for spring  
392 waters reacting with rocks of a deep reservoir that are comprised between 149 ±11 °C and  
393 325 ±21 °C. The lowest value, given by the silica geothermometer, is probably  
394 underestimated because of silica precipitation during thermal water cooling (Verma and  
395 Santoyo, 1997). The highest value, given by Na/Li geothermometers, is overestimated  
396 because Li concentrations in the fluids are higher than those used for calibrations (Sanjuan  
397 et al., 2014). We thus retain a range of temperature between 200 and 250 °C obtained using  
398 δ<sup>7</sup>Li (200 ±25 °C; Millot et al., 2010) and Na/K (228 ±9 °C and 205 ±12 °C; Verma and  
399 Santoyo, 1997; Santoyo and Diaz-Gonzalez, 2010) geothermometers, as the maximum  
400 temperature encountered by the water through the faults of the Pastos Grandes caldera.

401

402

#### 4.5 Chemical composition of the water

403

404 As extensively demonstrated in previous papers (Roche et al., 1991; Moquet et al., 2011),  
 405 we assumed the atmospheric contribution to groundwater chemistry as negligible in this  
 406 region and did not correct the data from this contribution. Elemental concentrations  
 407 reported in this study are represented and interpreted together with those from previous  
 408 studies of Laguna Pastos Grandes (Ballivian and Risacher, 1981; Hurlbert and Chang,  
 409 1984; Risacher and Fritz, 1991; Jones and Renaut, 1994). Spring waters have higher  
 410 salinity (~14 g/L) than streams (0.09 g/L) and homogeneous  $\delta^{37}\text{Cl}$  values of  $0.25\pm 0.03\%$   
 411 ( $n=12$ ; Table A4). The Piedmont spring is the only exception with a relatively low salinity  
 412 of 1.9 g/L. The brines from the southeastern part of the laguna are more saline than the  
 413 water sources (256 g/L; Table 2).

414 Most of the waters show charge balances better than  $\pm 8\%$  (Table 2), which denote a  
 415 negligible influence of potential organic charges to the ionic balance. Due to higher  
 416 sensitivity of low concentration samples to analytical errors, one stream sample shows a  
 417 charge balance of  $-26\%$  corresponding to a low anion excess of 0.41 mM.

418 Sodium and chloride are the dominant ions in spring waters, with average concentrations  
 419 of 173 and 203 mM, respectively. With a Ca:Mg molar ratio ranging from 1.9 to 2.4, spring  
 420 waters are enriched in Ca relative to Mg. Hydrothermal springs show similar relative ion  
 421 concentrations suggesting that a common origin and common processes constrained the  
 422 chemistry of their major elements (Fig. 5a). Their Ca:alkalinity molar ratio is favorable to  
 423 the precipitation of large amounts of calcite (with a ratio of almost one Ca for two C).  
 424 Compared with the hydrothermal springs, the Piedmont spring is diluted by surface waters.  
 425 As for the laguna brine, it presents relative ion concentrations similar to those of the  
 426 hydrothermal springs but with lower alkalinity (Fig. 5b).

427

#### 4.6 $\delta^7\text{Li}$ , $\delta^{11}\text{B}$ and $^{87}\text{Sr}/^{86}\text{Sr}$ in waters compared with surrounding rocks

428 *Table 3. Chemical and isotopic data available for dacites, andesites and ignimbrites from*  
 429 *Laguna Pastos Grandes. Data in italic are from previous studies.*

Rock type	Ca/Na	Mg/Na	Li (ppm) $\pm 0.3$ 1SD	$\delta^7\text{Li}$ (‰)	B (ppm) $\pm 0.3$ 1SD	$\delta^{11}\text{B}$ (‰)	Sr (ppm) $\pm 3$ 1SD	$^{87}\text{Sr}/^{86}\text{Sr}$
Ignimbrite	0.61	0.30	66.9	$-3.33\pm 0.47$	54	$-7.79\pm 0.21$	330	0.725764
Dacite 1	0.70	0.45	147.4	$-5.82\pm 0.12$	60	$-14.88\pm 0.21$	351	0.707906
Dacite 2	0.87	0.36	80.2	$-5.43\pm 0.35$	30	$-13.70\pm 0.15$	464	0.706951
Andesite 1	1.69	1.50	279.7	$-5.11\pm 0.38$	144	$-13.57\pm 0.09$	690	0.705835
Andesite 2	2.13	1.61	147.8	$-9.22\pm 0.15$	116	$-13.89\pm 0.10$	706	0.706206
<i>Ignimbrite (Kaiser, 2014)</i>								<i>0.708173</i>
<i>Ignimbrite (Kaiser, 2014)</i>								<i>0.708040</i>
<i>Cenomanian-Turonian carbonates (McArthur et al., 1994)</i>								<i>0.707298-0.707428</i>
<i>Modern marine evaporites (Pierret et al., 2001)</i>								<i>0.708940</i>

430

431 Thermal springs show homogeneous  $^{87}\text{Sr}/^{86}\text{Sr}$  values slightly more radiogenic than cold  
 432 streams with average values of  $0.70839\pm 0.00002$  and  $0.70780\pm 0.00021$ , respectively. In

433 the eastern part of the laguna, the perennial lake has a  $^{87}\text{Sr}/^{86}\text{Sr}$  value of 0.70833, slightly  
434 lower than thermal spring water values. As expected, all waters are within the range  
435 reported for dacites ( $0.70890\pm 0.00238$ ; Cortecci et al., 2005) and andesites  
436 ( $0.70763\pm 0.00161$ ; Cortecci et al., 2005) of the Andean Central Volcanic Zone. Our dataset  
437 is also compared with andesites, dacites and rhyolitic ignimbrites sampled in the vicinity  
438 of Laguna Pastos Grandes (Table 3). Sr isotope ratios of streams are between those of  
439 Pastos Grandes ignimbrites and dacites, whereas springs and brines show compositions  
440 similar to ignimbrites (Fig. 6a). The  $^{87}\text{Sr}/^{86}\text{Sr}$  value of Cenomanian-Turonian marine  
441 carbonates, considered as the last open marine period in the central Andes (Deconinck et  
442 al., 2000), is much lower than the values of the thermal springs (with  $^{87}\text{Sr}/^{86}\text{Sr} = 0.7073$ -  
443  $0.7074$ ; McArthur et al., 1994).

444 Boron and lithium isotopic compositions of Pastos Grandes waters are also clearly different  
445 from seawater composition ( $\delta^{11}\text{B} = 39.6\text{‰}$  and  $\delta^7\text{Li} = 31.0\text{‰}$ ; Boschetti et al., 2017).  $\delta^{11}\text{B}$   
446 and  $\delta^7\text{Li}$  values increase between rock and water samples in the following order: volcanic  
447 rocks < hydrothermal springs = lake brines < surface runoff. Pastos Grandes' thermal  
448 waters and brine present  $\delta^{11}\text{B}$  and  $\delta^7\text{Li}$  values around  $-5.5\pm 1.1\text{‰}$  and  $+4.1\pm 1.0\text{‰}$ ,  
449 respectively (Fig. 6b). In comparison, one stream displays more positive values for both  
450  $\delta^{11}\text{B}$  and  $\delta^7\text{Li}$ , at 0 and 10.9‰, respectively, whereas surrounding volcanic rocks are more  
451 negative, with  $\delta^{11}\text{B}$  between -14.9 and -7.8‰ and  $\delta^7\text{Li}$  between -9.2 and -3.3‰ (Fig. 6b;  
452 Table 3). In the study area, volcanic rocks have high Li and B concentrations (67–280 ppm  
453 of Li and 30–144 ppm of B) and isotopic compositions depleted in  $^7\text{Li}$  and  $^{11}\text{B}$  compared  
454 to the range of values for the Andean volcanic arc: 3-9 ppm of Li with  $-6.4 < \delta^7\text{Li} < -4.5\text{‰}$   
455 (Chan et al., 2002) and 6-60 ppm of B with  $-7 < \delta^{11}\text{B} < +4\text{‰}$  (Rosner et al., 2003). Boron  
456 isotopic compositions of Pastos Grandes volcanic rocks are slightly higher than the average  
457 continental crust, estimated by Chaussidon and Albarède (1992) between -15 and -10‰.

#### 458 **4.7 Thermodynamic model**

459 We compared the average spring water composition and the water chemistry obtained  
460 using PHREEQC modeling of volcanic bedrock alteration at 200-250 °C and  $\text{CO}_2$  partial  
461 pressure varying between 10 and 100 bar (typical of  $\text{CO}_2$ -rich geothermal systems;  
462 Lowenstern, 2001). The objective was to determine if the observed concentrations of major  
463 cations (Ca, Mg, K, Na and Si) can be reached by dissolution of the volcanic rocks (Table  
464 A5, see Appendix for the PHREEQC model) without input of ancient marine sediments.  
465 The mineralogy of the volcanic rocks surrounding Laguna Pastos Grandes was modeled  
466 with the following suite of minerals from the Thermoddem database (details in Appendix):

- 467 – Albite for the source of Na
- 468 – Anorthite for Ca
- 469 – Pargasite for Mg
- 470 – Quartz for Si
- 471 – Sanidine for K

472 In all models tested, the Si and DIC are higher than in the spring water. Ca, Mg, K and Na  
473 concentrations are best reproduced at 225 °C and 20 bar of  $\text{CO}_2$  (SI=1.3; Fig. A2). To  
474 adjust the Cl concentration in the water, we tried different Cl sources: pure magmatic  $\text{Cl}_2(\text{g})$   
475 or halite. Modeling results were inconclusive with pure magmatic  $\text{Cl}_2(\text{g})$  but consistent  
476 with halite, suggesting that the salinity of the spring water is provided by halite dissolution.  
477 As halite is commonly associated with gypsum in the sedimentary series of the Andean  
478 region, we also added anhydrite to the bedrock composition in the model. Despite this, the

479 main source of Ca in the spring waters remains anorthite (Table A5). All minerals were  
480 considered in the calculation as infinite reservoirs, except halite, which was fixed by the  
481 average Cl concentration in the spring water (239 mM).

## 482 **5. Discussion**

483 Laguna Pastos Grandes is a calcic-type salar characterized by Na-Ca-Cl brines that can,  
484 according to thermodynamic models, lead to the precipitation of calcite, the first mineral  
485 of the evaporation pathway before gypsum and ulexite (Hardie and Eugster, 1970; Risacher  
486 and Fritz, 2009). Although 19% of the salars in Bolivia (n=6) and 24% in Chile (n=12,  
487 Table A6) are calcic-type salars, massive calcite precipitation is only observed in Laguna  
488 Pastos Grandes. Gypsum, mirabilite (Na<sub>2</sub>SO<sub>4</sub>), halite and ulexite dominate the other calcic  
489 salars. This means that, in addition to the Ca<sup>2+</sup> concentration, at least one parameter varies  
490 among the Andean salars and controls the magnitude of calcite precipitation in Laguna  
491 Pastos Grandes. The precipitation of carbonate minerals is complicated by  
492 biomineralization processes (mediated here by microorganisms; Jones and Renaut, 1994)  
493 and reaction kinetics in a near-surface continental environment (with ionic interactions,  
494 variable substrates, fluctuating pH, organic molecules and gas-phase interactions; Alonso-  
495 Zarza and Tanner, 2010). Still, the fundamental reasons why calcite precipitates in  
496 significant amounts are that i) Ca<sup>2+</sup><sub>(aq)</sub> and CO<sub>3</sub><sup>2-</sup><sub>(aq)</sub> are supplied in sufficient concentrations  
497 by water inputs and ii) surface processes allow the pH to increase, thereby dynamically  
498 sustaining supersaturation relative to calcite. At Laguna Pastos Grandes, we expect these  
499 processes to be related to dissolved CO<sub>2</sub> losses, such as degassing, salting-out by  
500 evaporation and photosynthesis. Our investigations therefore focused on the origin of CO<sub>2</sub>  
501 and Ca enrichment in water inputs.

### 502 **5.1 Origin of CO<sub>2</sub> and N<sub>2</sub> in thermal spring gases**

503 The thermal springs of Laguna Pastos Grandes discharge not only thermal waters but also  
504 gases that are essentially mixtures of CO<sub>2</sub> and N<sub>2</sub> (Table 1). This is common in the Central  
505 Andes (Spiro et al., 1997). Changes in the relative proportions of CO<sub>2</sub> and N<sub>2</sub> gases between  
506 sources in Laguna Pastos Grandes can be partly attributed to changes in the contribution  
507 from Air Saturated Waters (ASW) to the hydrothermal system. Indeed, the <sup>40</sup>Ar/<sup>36</sup>Ar mean  
508 value of 289 in thermal springs is close to the air value of 295 (Nier, 1950) and their  
509 Atmosphere-Derived Noble Gases abundances (ADNG: <sup>20</sup>Ne and <sup>36</sup>Ar) normalized to air  
510 indicate that the atmospheric component in thermal springs (including O<sub>2</sub> and the  
511 atmospheric proportion of N<sub>2</sub>) derives from ASW and not from air-contamination during  
512 sampling (Fig. 3).

513  
514 Despite the ASW component, the mean R<sub>C</sub>/R<sub>A</sub> value of 3.79 ± 0.08 (Fig. 3, Table 1)  
515 indicates the presence of mantle-derived helium in the ascending hydrothermal gas. Our  
516 helium isotope results complement and confirm previous data from the central Andes,  
517 including an isolated analysis at Laguna Pastos Grandes (Fig. A3; Hilton et al., 1993; Hoke  
518 et al., 1994). Assuming that pure mantle-derived helium is characterized by R<sub>C</sub>/R<sub>A</sub> ~8, we  
519 calculated that about 47 % of the helium in Laguna Pastos Grandes is of mantle origin  
520 (using the calculations described in Hoke et al., 1994; Table 1), whereas it does not exceed  
521 20% in other gas sources on the Altiplano. In the Western Cordillera, however, the supply  
522 of mantle helium reaches 69% at the Isluga volcano in Chile, 300 km north of Laguna  
523 Pastos Grandes (Hoke et al., 1994). In addition, the highest temperature of salar springs on

524 the Altiplano was recorded at Laguna Pastos Grandes, at 75 °C by Jones and Renaut (1994)  
525 and at 46 °C in this study (Table A6). For comparison, the maximum temperature recorded  
526 in the Western Cordillera is about 87 °C (Puchuldiza salar, northern Chile; Risacher et al.,  
527 2011). Therefore, the strong mantle influence in Laguna Pastos Grandes is probably due to  
528 its proximity to the active volcanic arc of the Western Cordillera (Table A6; Springer and  
529 Förster, 1998).

530

531 The average  $\delta^{13}\text{C}$  value of  $\text{CO}_2 \sim -11.1 \pm 0.1\text{‰}$  is lower than the typical value of a magmatic  
532 mantle-derived  $\text{CO}_2$  source (between -9 and -4‰; Hoefs, 1980) that would be expected  
533 based on He results. Two hypotheses can be proposed to explain this low value: a  
534 contribution of  $\text{CO}_2$  from sedimentary sources, i.e., organic carbon with  $\delta^{13}\text{C} < -20\text{‰}$   
535 (Hoefs, 1980), or carbonate precipitation during fluid ascent. To trace the origin of the  $\text{CO}_2$ ,  
536  $\delta^{13}\text{C}$  values are generally interpreted in relation to  $\text{CO}_2/{}^3\text{He}$  values (Sano and Marty, 1995).  
537 In order to avoid the effects of hydrothermal degassing and liquid-vapor partitioning that  
538 could have significantly affected the  $\delta^{13}\text{C}$  and  $\text{CO}_2/{}^3\text{He}$  values of the gas, we determined  
539 the  $\text{CO}_2/{}^3\text{He}$  composition at threshold P-T degassing conditions, using fluid phase  
540 equilibrium calculations applied to our system ( $\text{H}_2\text{O}-\text{NaCl}-\text{CO}_2-\text{N}_2-\text{O}_2-\text{He}-\text{Ne}-\text{Ar}$ ;  
541 Rouchon et al., 2016). We assumed that all gaseous  $\text{CO}_2$  was exsolved at a single  
542 supersaturation depth and that there was no carbonate precipitation (which would decrease  
543 the  $\text{CO}_2/{}^3\text{He}$  value). The best results were obtained with an initial meteoric water recharge  
544 at high altitude, i.e. 5500 m, and a temperature of 0 °C. This is consistent with the  $\delta^{18}\text{O}$  and  
545  $\delta^2\text{H}$  relationship in the spring waters, which suggests that the geothermal reservoir is fed  
546 during the wet season by meteoric water of rainfall isotopic composition (i.e.,  $\delta^{18}\text{O}$  of -  
547 16‰ and  $\delta^2\text{H}$  of -123‰; Fig. 4 and Table A2 for values). Snow deposited during the dry  
548 season has different isotopic compositions (minimum  $\delta^{18}\text{O}$  of -6.8‰ and  $\delta^2\text{H}$  of -30.3‰).  
549 Considering a local geotherm of 45 °C/km (Rothstein and Manning, 2003), we calculated  
550 between 17 and 49%  $\text{CO}_2$  exsolution at a depth of about 25-35 m (at 2.5-3.5 bar) in the  
551 different springs (Table 1). Before degassing, the  $\text{CO}_2/{}^3\text{He}$  values were higher than those  
552 measured at the surface and ranged from  $4.7 \cdot 10^8$  to  $2.9 \cdot 10^9$ . These values are in the range  
553 or slightly lower than the mantle value of  $2 \cdot 10^9$  (Marty and Jambon, 1987). The depletion  
554 of  $\text{CO}_2$  relative to  ${}^3\text{He}$  in fluids could be consistent with carbonate precipitation during the  
555 geothermal fluid ascent. Since carbonates are enriched in  ${}^{13}\text{C}$  relative to original  $\text{CO}_2$ , this  
556 would also explain why the remaining  $\text{CO}_2$  in the gas is depleted in  ${}^{13}\text{C}$  (Ray et al., 2009).

557

558 Even so, we cannot completely rule out a minor contribution from thermal or microbial  
559 decomposition of organic matter in the underlying but unknown sedimentary rocks,  
560 perhaps accompanied to some extent by carbonate dissolution, which could account for the  
561 slight shift towards negative  $\delta^{13}\text{C}_{\text{CO}_2}$  values relative to the mantle. Likewise, the  $\delta^{15}\text{N}$   
562 values between 2.3 and 6.4‰ could reflect a crustal (mean  $\delta^{15}\text{N} = +7\text{‰}$ ; e.g. Sano et al.,  
563 1998) contribution mainly generated by biological or thermal degradation (Boyd, 2001).  
564 Although stratovolcanoes and their products dominate the South Lipez landscape of the  
565 Altiplano (e.g. de Silva and Francis, 1991), volcanic rocks probably overlain (Ludington  
566 et al., 1975) or incorporated (Risacher and Alonso, 2001) Cretaceous and Early Tertiary  
567 clastic to evaporitic sediments. Alternatively, as this region is close to the subduction zone  
568 of the Nazca plate under the South American plate (the slab being located at a depth of  
569 ~150-km below the Altiplano; Hoke et al., 1994; Kay and Coira, 2009), organic carbon and  
570 nitrogen could be remobilized from the slab by metamorphism (Gorman et al., 2006) and  
571 transported through primary melts into crustal intrusions. This hypothesis is supported by

572 the high Li concentrations and light  $\delta^7\text{Li}$  recorded in volcanic lava flows surrounding  
573 Laguna Pastos Grandes (compared with MORB composition representing the upper  
574 mantle,  $\delta^7\text{Li} = 3.7\%$ ; Misra and Froelich, 2012). It can only be interpreted as the addition  
575 of highly-negative  $\delta^7\text{Li}$  slab-derived fluids to the mantle wedge beneath our study area  
576 (Fig. 7; Chan et al., 2002). Boron is also highly concentrated in the volcanic rocks of the  
577 area (30-144 ppm) and could come from the same source as Li. However,  $\delta^{11}\text{B}$  values,  
578 between -14 and -8‰, are more negative than the lowest value of the slab-derived fluids  
579 predicted for the Andes (-2.8‰; Rosner et al., 2003). Boron is more volatile than lithium,  
580 and light  $\delta^{11}\text{B}$  values are commonly observed in magmatic rocks (Chaussidon and  
581 Albarède, 1992) due to magma degassing effects, which produce  $^{11}\text{B}$  depletion in the  
582 residual melt (Jiang and Palmer, 1998).

583

## 584 **5.2 Hydrological history of spring water**

585

586 The spring waters in Andean salars have previously been suggested to originate from the  
587 recycling of lake brines that continuously infiltrate through their bottom sediments  
588 (Risacher and Fritz, 1991; Risacher et al., 2003; Risacher and Fritz, 2009). The origin (and  
589 evolution) of the spring waters in Laguna Pastos Grandes can be assessed using their water  
590 isotopic composition. Spring waters lie on the local Ground and Spring Water Line  
591 (LGSWL) with slightly more positive  $\delta^{18}\text{O}$  and  $\delta^2\text{H}$  values than the local rainfall (Fig. 4),  
592 indicating that hydrothermal springs are genetically linked to meteoric waters. The slight  
593 enrichment in both  $^{18}\text{O}$  and  $^2\text{H}$  relative to meteoric water may imply either evaporative  
594 enrichment prior to infiltration at high altitude (Bershaw et al., 2016) or vapor loss during  
595 the ascent of thermal fluids (Cortecchi et al., 2005). In comparison, the laguna brine is highly  
596 enriched in  $^{18}\text{O}$  and  $^2\text{H}$ , ruling out the hypothesis of a significant recharge of the springs by  
597 infiltration of the laguna brine. In addition, the Cl/Br values of spring waters cannot be  
598 explained by a dilution of recycled brines by mixing with groundwater or meteoric water  
599 (Fig. 5c). We thus suggest that the solutes in the spring waters more likely derive from the  
600 alteration of the bedrock minerals.

601

## 601 **5.3 Volcanic bedrock alteration at high temperature and $\text{pCO}_2$**

602  $\delta^7\text{Li}$  and Na/K geothermometers applied to spring waters indicate that the meteoric water  
603 reached a maximum temperature of 200-250 °C after infiltration. Due to the high mantle-  
604 derived  $\text{CO}_2$  flux delivered in thermal springs, the estimated  $\text{pCO}_2$  in these waters (between  
605 3 and 389 mbar estimated by PHREEQC; Table 2) spans the range and even exceeds the  
606  $\text{pCO}_2$  in spring waters of the Altiplano and Western Cordillera at 40 – 120 and 10 – 340  
607 mbar, respectively (Morteani et al., 2014). This  $\text{CO}_2$  enrichment can acidify thermal waters  
608 to a pH ~5 favoring bedrock minerals dissolution and hence thermal waters enrichment in  
609 solutes, especially in Ca. To test this hypothesis, we performed a series of PHREEQC  
610 simulations to determine the water composition resulting from the alteration of the volcanic  
611 bedrock with possible evaporites (halite, gypsum and anhydrite) from a meteoric water at  
612 200, 225 and 250 °C and varying  $\text{CO}_2$  partial pressures and compared the results to the  
613 average spring water composition (Table A5; Fig. A2).

614

615 The best results for Ca, Mg and K concentrations in spring waters were obtained by  
616 alteration of volcanic minerals at a temperature of 225 °C and at 20 bar of  $\text{CO}_2$  (Fig. A2).  
617 This amount of  $\text{CO}_2$  is compatible with the proximity of an ancient pre-eruptive magma  
618 reservoir at a depth of ~3 km as proposed by de Silva and Kay (2018). Under these

619 conditions, the main source of Ca in the water is the dissolution of Ca-rich feldspars rather  
620 than anhydrite (Table A5). These results are corroborated by Sr isotope data, which suggest  
621 that local meteoric waters interact with the host volcanic rocks (dacite, andesite and  
622 rhyolitic ignimbrite) rather than with ancient marine carbonates (Fig. 6a). Similarly, the  
623  $\delta^7\text{Li}$  and  $\delta^{11}\text{B}$  values of the thermal waters and laguna brine are closer to those of the  
624 surrounding volcanic rocks than to those of seawater (Fig. 6b).  $\delta^7\text{Li}$  values measured in  
625 waters are on average 8‰ higher than those measured in the surrounding rocks. This  
626 fractionation corresponds to the equilibrium isotopic fractionation between water and  
627 weathered volcanic rocks at high temperature ( $200\pm 25^\circ\text{C}$ ; Millot et al., 2010). On the other  
628 hand, the average 7‰ positive  $\delta^{11}\text{B}$  shift between springs and volcanic rocks can be  
629 explained either by adsorption of B on mineral surfaces during the ascent and cooling of  
630 hydrothermal fluid to the spring vent (Louvat et al., 2014b) or by the preferential  
631 incorporation of light B during carbonate precipitation (Vengosh et al., 1991).

632  
633 Interestingly, the hydrothermal fluid obtained with these simulations is over-saturated with  
634 several carbonate minerals ( $\text{SI}_{\text{calcite}}=1.23$ ,  $\text{SI}_{\text{dolomite}}=3.03$ ,  $\text{SI}_{\text{magnesite}}=2.02$ ), which supports  
635 the hypothesis (based on  $\text{CO}_2/{}^3\text{He}$  and  $\delta^{13}\text{C}$  data) that carbonate could have precipitated  
636 during fluid ascent. The higher Si concentration obtained in our simulations compared with  
637 those measured in spring waters together with the low temperature given by the  $\text{SiO}_2$   
638 geothermometer are also consistent with the precipitation of silica during fluid ascent.  
639 Furthermore, the simulations suggest that the salinity of the spring water most likely results  
640 from the dissolution of halite deposits. This interpretation is confirmed by the  
641 homogeneous  $\delta^{37}\text{Cl}$  mean value of the springs at  $0.25\pm 0.03\text{‰}$  ( $n=12$ ; Table A4), as  
642 expected for halite precipitation in equilibrium with seawater at  $25^\circ\text{C}$  ( $\delta^{37}\text{Cl} = 0.30 \text{‰}$ ;  
643 Eggenkamp et al., 2016). It indicates that over time, multiple cycles of halite precipitation  
644 and dissolution without new Cl inputs to the laguna have homogenized the Cl isotopic  
645 composition of the laguna brine and salts. Therefore, we can assume that Na and Cl  
646 originate from marine evaporites deposited during the last Cenomanian-Turonian marine  
647 period and later remobilized in Cretaceous and Tertiary continental deposits (Deconinck et  
648 al., 2000) that could have been either overlain by volcanic rocks or incorporated by  
649 volcanic eruptions as suggested by Risacher and Alonso (2001) for gypsum. This is also  
650 consistent with equimolar Cl and Na concentrations of these waters, typical of halite  
651 leaching (Fig. A4).

652  
653  
654

#### 5.4 How is Laguna Pastos Grandes unique?

655 Ca:alkalinity molar ratios of waters of Laguna Pastos Grandes show that stream waters and  
656 mixed sources (Piedmont) are too diluted to contribute significantly to the growth of the  
657 carbonate platform. They also show that the laguna brine, which largely derives from  
658 spring waters (as suggested by chemical and isotopic data; Figs. 4, 5, 6), has been depleted  
659 in carbonate relative to Ca. Therefore, only the thermal springs have the potential to  
660 precipitate calcite massively (Fig. 5b). Most of the salars in the Central Andes are fed by  
661 thermal spring (60% in Bolivia and 78% in Chile) enriched in solutes compared with  
662 streams and regional groundwater (Table A6; Risacher and Fritz, 1991; Risacher et al.,  
663 2011). Modern carbonates are, however, absent or minor in these systems and generally  
664 precipitated as the first mineral of a more developed evaporitic sequence (Risacher and  
665 Fritz, 2009). Laguna Pastos Grandes is unique in this respect, as it hosts a  $\sim 40 \text{ km}^2$  recent-  
666 to-modern carbonate platform spatially associated with thermal springs. There is a



667 remarkable mantle influence on these springs' temperature and gas composition, as well as  
668 on their solute enrichments (the highest of the Central Andes) with an average salinity of  
669 14 g/l (Fig. 7; Table A6). This highlights the high water-rock reactivity of the hydrothermal  
670 system of Laguna Pastos Grandes compared to other salars, due to the high flow of CO<sub>2</sub>  
671 gas from the mantle. Furthermore, the singularity of this laguna is probably related to the  
672 mineralogy of the volcanic bedrock since calcic-type salars are limited to the Andean  
673 region. For example, Chilean volcanic rocks are known to be enriched in sulfides (Risacher  
674 and Alonso, 2001) and could be responsible for the greater abundance of sulfate-type salars  
675 (65%) compared to calcic-type salars.

## 676 **6. Conclusion and perspectives**

677 Bolivian and Chilean salars belong to broadly the same climatic and geological  
678 environment (Risacher and Fritz, 2009). Nevertheless, they vary widely in terms of  
679 chemistry and salt types mostly as a result of local variations in their fluid sources. In this  
680 study, we have shown that the western part of Laguna Pastos Grandes, characterized by  
681 abundant carbonate deposits, is mainly fed by thermal spring water, with minor  
682 contributions from rainfall and surrounding streams. We demonstrated that these spring  
683 waters, over-saturated with calcite, have been enriched in calcium and carbonate alkalinity  
684 by the alteration of the volcanic bedrock under high CO<sub>2</sub> partial pressure and a temperature  
685 of 200-250°C. The magmatic CO<sub>2</sub> and the high heat flow that drive the fluid circulation to  
686 the surface are probably due to a shallow pre-eruptive magma chamber as proposed by de  
687 Silva et al. (2006) and de Silva and Kay (2018) (i.e. at a typical depth of ~5 km; Fig. 7).  
688 We propose that this doping in magmatic CO<sub>2</sub> and the mineralogy of the volcanic bedrock  
689 are the reason for the large volumes of carbonates compared to most other modern Andean  
690 salars.

691  
692 This configuration is not exclusive to Laguna Pastos Grandes system and can be found in  
693 many continental extensional settings (e.g. in Afar) where we posit, by analogy, that the  
694 same mechanisms are involved in the genesis of continental carbonate deposits in volcanic  
695 provinces. As identified in this study, the main factors that favor a significant production  
696 of carbonates would be a deep source of CO<sub>2</sub> and a Ca-rich volcanic basement allowing  
697 the following processes to occur:

- 698 i. Alteration of a sulfide-poor volcanic bedrock containing Ca-enriched minerals  
699 (usually feldspars) at high pCO<sub>2</sub> (20 bar) and high temperature (225°C), leading to cationic  
700 enrichment of the waters and yielding calcic type hydrothermal waters.
- 701 ii. At the surface, CO<sub>2</sub> degassing that leads to a pH increase and results in carbonate  
702 precipitation. CO<sub>2</sub> loss may also be driven by photosynthesis.
- 703 iii. High evaporation rates, increasing both the solute concentrations above calcite  
704 saturation and the associated CO<sub>2</sub> salting-out, and resulting in a pH increase.

705  
706 Laguna Pastos Grandes is therefore a unique natural laboratory that hosts a great diversity  
707 of carbonate facies (including pisoliths, ooids, muds and microbialites; Risacher and  
708 Eugster, 1979; Jones and Renaut, 1994; Bougeault et al., 2019), sometimes remarkably  
709 similar to ancient equivalents such as Cretaceous Presalt carbonates (Terra et al., 2010;  
710 Tosca and Wright, 2015). This laguna could, therefore, be further used to identify the biotic  
711 and/or abiotic controls involved in the formation of these carbonate deposits. Indeed,  
712 microbial mats and thin, dark, mucilaginous films locally coating the pool floors and  
713 pisolith surfaces in Laguna Pastos Grandes (described by Jones and Renaut, 1994 and

714 Bougeault et al., 2019) could also influence both the carbonate precipitation and fabrics  
715 (Pace et al., 2018; Gomez et al., 2018). Comprehensive geochemical, mineralogical and  
716 biodiversity studies are underway to characterize the links between physicochemical  
717 parameters, microbial communities and the diversity of carbonate fabrics observed in  
718 Laguna Pastos Grandes. These results will provide additional insight into the nature of the  
719 biosignatures preserved in microbialites's mineralogy and fabrics and allow us to further  
720 interpret the sedimentary record on our planet.

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## 734 **References**

- 735 Alonso-Zarza A. M. and Tanner L. H. (2010) Carbonates in continental settings: Facies,  
736 environments, and processes. *Dev. Sedim.* **61**, pp. 378.
- 737 Assayag N., Jézéquel D., Ader M., Viollier E., Michard G., Prévot F., and Agrinier P.  
738 (2008) Hydrological budget, carbon sources and biogeochemical processes in Lac Pavin  
739 (France): constraints from  $\delta^{18}\text{O}$  of water and  $\delta^{13}\text{C}$  of dissolved inorganic carbon. *Appl.*  
740 *Geochem.* **23**(10), 2800-2816.
- 741 Ballivian O. and Risacher F. (1981) Los salares del altiplano boliviano: métodos de  
742 estudio y estimación económica. IRD Editions.
- 743 Bershaw J., Saylor J.E., Garzzone C.N., Leier A. and Sundell K.E. (2016) Stable isotope  
744 variations ( $\delta^{18}\text{O}$  and  $\delta^2\text{H}$ ) in modern waters across the Andean Plateau. *Geochim. et*  
745 *Cosmochim. Acta* **194**, 310–324.
- 746 Blanc P., Lassin A., Piantone P., Azaroual M., Jacquemet N., Fabbri A., and Gaucher  
747 E.C. (2012) Thermoddem: A geochemical database focused on low temperature  
748 water/rock interactions and waste materials. *Appl. Geochem.* **27**(10), 2107-2116.
- 749 Boschetti T., Cortecchi G., Barbieri M. and Mussi M. (2007) New and past geochemical  
750 data on fresh to brine waters of the Salar de Atacama and Andean Altiplano, northern  
751 Chile. *Geofluids* **7**(1), 33-50.
- 752 Boschetti T., Toscani L., Iacumin P. and Selmo E. (2017) Oxygen, Hydrogen, Boron and  
753 Lithium Isotope Data of a Natural Spring Water with an Extreme Composition: A Fluid  
754 from the Dehydrating Slab? *Aquat. Geochem.* **23**(5-6), 299-313.
- 755 Bougeault C., Vennin E., Durllet C., Muller E., Mercuzot M., Chavez M., Gérard E., Ader  
756 M., Virgone A. and Gaucher E. C. (2019). Biotic–Abiotic Influences on Modern Ca–Si–  
757 Rich Hydrothermal Spring Mounds of the Pastos Grandes Volcanic Caldera (Bolivia).  
758 *Minerals* **9**(6), 380.
- 759 Boyd S. R. (2001). Nitrogen in future biosphere studies. *Chem. Geol.* **176**(1-4), 1-30.

760 Chaffaut I., Coudrain-Ribstein A., Michelot J. L. and Pouyau B. (1998) Précipitations  
761 d'altitude du Nord-Chili, origine des sources de vapeur et données isotopiques. *Bull. Inst.*  
762 *Fr. Etudes andines* **27**, 367-384 (in French).

763 Chan L.H., Edmond J.M., Thompson G. and Gillis K. (1992) Lithium isotopic  
764 composition of submarine basalts: implications for the lithium cycle in the oceans. *Earth*  
765 *Planet. Sci. Lett.* **108**, 151–160.

766 Chan L.H. and Kastner, M. (2000) Lithium isotopic composition of pore fluids and  
767 sediments in the Costa Rica subduction zone: implications for fluid processes and  
768 sediment contribution to arc volcanoes. *Earth Planet. Sci. Lett.* **183**, 275–290.

769 Chan L. H., Leeman W. P. and You C. F. (2002) Lithium isotopic composition of Central  
770 American volcanic arc lavas: implications for modification of subarc mantle by slab-  
771 derived fluids: correction. *Chem. Geol.* **182**(2-4), 293-300.

772 Chaussidon M. and Albarède F. (1992) Secular boron isotope variations in the continental  
773 crust: an ion microprobe study. *Earth Planet. Sci. Lett.* **108**(4), 229-241.

774 Chaussidon M. and Marty B. (1995) Primitive boron isotope composition of the mantle.  
775 *Science* **269**, 383–386.

776 Chetelat B., Liu C.-Q., Gaillardet J., Wang Q.L., Zhao Z.Q., Liang C.S., Xiao Y.K.  
777 (2009) Boron isotopes geochemistry of the Changjiang basin rivers. *Geochim.*  
778 *Cosmochim. Acta* **73**, 6084-6097.

779 Cortecchi G., Boschetti T., Mussi M., Lameli C. H., Mucchino C. and Barbieri M. (2005)  
780 New chemical and original isotopic data on waters from El Tatio geothermal field,  
781 northern Chile. *Geochim. J.* **39**(6), 547-571.

782 Deconinck J. F., Blanc-Valleron M. M., Rouchy J. M., Camoin G. and Badaut-Trauth D.  
783 (2000) Palaeoenvironmental and diagenetic control of the mineralogy of Upper  
784 Cretaceous–Lower Tertiary deposits of the Central Palaeo–Andean basin of Bolivia  
785 (Potosi area). *Sedim. Geol.* **132**(3-4), 263-278.

786 Dellinger M., Gaillardet J., Bouchez J., Calmels D., Louvat P., Dosseto A., Gorge C.,  
787 Alanoca L. and Maurice L. (2015) Riverine Li isotope fractionation in the Amazon River  
788 basin controlled by the weathering regimes. *Geochim. Cosmochim. Acta* **164**, 71-93.

789 De Hoog J. C. and Savov I. P. (2018) Boron isotopes as a tracer of subduction zone  
790 processes. In *Boron Isotopes* (eds Springer, Cham), pp. 217-247.

791 de Silva S. L. and Francis P. W. (1991) *Volcanoes of the Central Andes*. Springer Verlag,  
792 Berlin.

793 de Silva S., Zandt G., Trumbull R., Viramonte J. G., Salas G. and Jimenez N. (2006)  
794 Large ignimbrite eruptions and volcano-tectonic depressions in the Central Andes: a  
795 thermomechanical perspective. In: Trois, C., De Natale, G., Kilburn, C.R.J. (Eds.),  
796 *Mechanism of Activity and Unrest at Large Calderas*, vol. 269. Geol. Soc. London, Spec.  
797 Publ., pp. 47-63.

798 de Silva S. and Kay S.M. (2018) Turning up the Heat: High-Flux Magmatism in the  
799 Central Andes. *Elements* **14**, 245-250.

800 Durand N., Monger H. C., Canti M. G. and Verrecchia E. P. (2018) Calcium carbonate  
801 features. In *Interpretation of micromorphological features of soils and regoliths*. Elsevier.  
802 pp. 205-258.

803 Eggenkamp H. G. M., Bonifacie M., Ader M., and Agrinier P. (2016) Experimental  
804 determination of stable chlorine and bromine isotope fractionation during precipitation of  
805 salt from a saturated solution. *Chem. Geol.* **433**, 46-56.

806 Fritz P., Suzuki O., Silva C. and Salati E. (1981) Isotope hydrology of groundwaters in  
807 the Pampa Del Tamarugal, Chile. *J. Hydrol.* **53**, 161–184.

808 Gaillardet J. and Allègre C. J. (1995) Boron isotopic compositions of corals: Seawater or  
809 diagenesis record? *Earth Planet. Sci. Lett.* **136**(3-4), 665-676.

810 Godon A., Jendrzewski N., Eggenkamp H. G., Banks D. A., Ader M., Coleman M. L.  
811 and Pineau F. (2004) A cross-calibration of chlorine isotopic measurements and  
812 suitability of seawater as the international reference material. *Chem. Geol.* **207**(1-2), 1-  
813 12.

814 Gomez F. J., Kah L. C., Bartley J. K. and Astini R. A. (2014) Microbialites in a high-  
815 altitude Andean lake: multiple controls on carbonate precipitation and lamina accretion.  
816 *Palaios* **29**(6), 233-249.

817 Gomez F. J., Mlewski C., Boidi F. J., Farías M. E. and Gérard E. (2018) Calcium  
818 carbonate precipitation in diatom-rich microbial mats: the Laguna Negra hypersaline  
819 lake, Catamarca, Argentina. *J. Sedim. Res.* **88**(6), 727-742.

820 Gorman P. J., Kerrick D. M. and Connolly J. A. D. (2006) Modeling open system  
821 metamorphic decarbonation of subducting slabs. *Geochem. Geophys. Geosy.* **7**(4).

822 Gran, G. (1952). Determination of the equivalence point in potentiometric titrations. Part  
823 II. *Analyst* **77**(920), 661-671.

824 Hardie L. A. and Eugster H. P. (1970) The evolution of closed-basin brines. *Min. Soc.*  
825 *Am. Special Paper* **3**, 273-290.

826 Hilton D. R., Hammerschmidt K., Teufel S. and Friedrichsen H. (1993) Helium isotope  
827 characteristics of Andean geothermal fluids and lavas. *Earth Planet. Sci. Lett.* **120**(3-4),  
828 265-282.

829 Hoefs J. (1980) *Stable isotope geochemistry*. Berlin and Heidelberg, Springer Verlag.

830 Hoke L., Hilton D. R., Lamb S. H., Hammerschmidt K. and Friedrichsen H. (1994) <sup>3</sup>He  
831 evidence for a wide zone of active mantle melting beneath the Central Andes. *Earth*  
832 *Planet. Sci. Lett.* **128**(3-4), 341-355.

833 Hurlbert S. H. and Chang C. C. (1984) Ancient ice islands in salt lakes of the Central  
834 Andes. *Science* **224**(4646), 299-302.

835 Jiang S. Y. and Palmer M. R. (1998) Boron isotope systematics of tourmaline from  
836 granites and pegmatites; a synthesis. *Europ. J. Min.* **10**(6), 1253-1265.

837 Jones B. and Renaut R. W. (1994) Crystal fabrics and microbiota in large pisoliths from  
838 Laguna Pastos Grandes, Bolivia. *Sedimentology* **41**(6), 1171-1202.

839 Kaiser J. F. (2014) Understanding large resurgent calderas and associated magma  
840 systems: the Pastos Grandes Caldera Complex, southwest Bolivia. PhD thesis of Oregon  
841 State University.

842 Kay S. M. and Coira B. L. (2009) Shallowing and steepening subduction zones,  
843 continental lithospheric loss, magmatism, and crustal flow under the Central Andean  
844 Altiplano-Puna Plateau. *Backbone of the Americas: shallow subduction, plateau uplift,*  
845 *and ridge and terrane collision*, 204, 229.

846 Li L., Cartigny P. and Ader M. (2009) Kinetic nitrogen isotope fractionation associated  
847 with thermal decomposition of NH<sub>3</sub>: Experimental results and potential applications to  
848 trace the origin of N<sub>2</sub> in natural gas and hydrothermal systems. *Geochim. Cosmochim.*  
849 *Acta* **73**(20), 6282-6297.

850 Louvat P., Moureau J., Paris G., Bouchez J., Noireaux J., Gaillardet J. (2014a) A fully  
851 automated direct injection nebulizer (d-DIHEN) for MC-ICP-MS isotope analysis:  
852 application to boron isotope ratio measurements. *J. Anal. Atom. Spectrom.* **29**(9), 1698-  
853 1707.

854 Louvat P., Gayer E. and Gaillardet J. (2014b) Boron behavior in the rivers of Réunion  
855 island, inferred from boron isotope ratios and concentrations of major and trace elements.  
856 *Proced. Earth Plan. Sc.* **10**, 231-237.

857 Lowenstern J. B. (2001) Carbon dioxide in magmas and implications for hydrothermal  
858 systems. *Miner. Deposita* **36**(6), 490-502.

859 Ludington S., Orris G.J., Cox D.P., Long K.R. and Asher-Bolinden S. (1975) Mineral  
860 deposit models. In *Geology and Mineral Resources of the Altiplano and the Cordillera*  
861 *Occidental, Bolivia* (eds Bleiwas D. J. and Christiansen R. G.). U.S. Geol. Survey Bull.  
862 pp. 63-224

863 Luddington S., Orris G.J., Cox D.P., Long K.R. and Asher-Bolinder S. (1992) Mineral  
864 deposit models. In *Geology And Mineral Resources Of The Altiplano and Cordillera*  
865 *Occidental, Bolivia* (eds by U.S. Geological Survey and Servicio Geolbgico de Bolivia).  
866 Bull. US geol. Surv. 1975, pp. 63-89.

867 Marschall H. R. (2018) Boron isotopes in the ocean floor realm and the mantle. In *Boron*  
868 *Isotopes* (eds Springer, Cham), pp. 189-215.

869 Marty B. and Jambon A. (1987) <sup>3</sup>He in volatile fluxes from the solid Earth: Implications  
870 for carbon geodynamics. *Earth Plan. Sci. Lett.* **83**, 16-26.

871 McArthur J. M., Kennedy W. J., Chen M., Thirlwall M. F. and Gale A. S. (1994)  
872 Strontium isotope stratigraphy for Late Cretaceous time: direct numerical calibration of  
873 the Sr isotope curve based on the US Western Interior. *Palaeoeco. Palaeoclim.*  
874 *Palaeoeco.* **108**(1-2), 95-119.

875 Millot R., Guerrot C. and Vigier N. (2004) Accurate and high-precision measurement of  
876 lithium isotopes in two reference materials by MC-ICP-MS. *Geostand. Geoanal. Res.*  
877 **28**(1), 153-159.

878 Millot R., Scaillet B. and Sanjuan B. (2010) Lithium isotopes in island arc geothermal  
879 systems: Guadeloupe, Martinique (French West Indies) and experimental approach.  
880 *Geochim. Cosmochim. Acta* **74**, 1852-1871.

881 Misra S. and Froelich P. N. (2012) Lithium isotope history of Cenozoic seawater:  
882 changes in silicate weathering and reverse weathering. *Science* **335**(6070), 818-823.

883 Moquet J. S., Crave A., Viers J., Seyler P., Armijos E., Bourrel L., Chavarri E.N, Lagane  
884 C., Laraque A., Lavado Casimiro W.S., Pombosa R., Noriega L., Vera A. and Guyot J.L.  
885 (2011) Chemical weathering and atmospheric/soil CO<sub>2</sub> uptake in the Andean and  
886 Foreland Amazon basins. *Chem. Geol.* **287**(1-2), 1-26.

887 Moreira M., Rouchon V., Muller E. and Noirez S. (2018) The xenon isotopic signature of  
888 the mantle beneath Massif Central. *Geochem. Perspect. Lett.* **6**, 28-32.

889 Moriguti T. and Nakamura E. (1998) Across-arc variation of Li isotopes in lavas and  
890 implications for crust/mantle recycling at subduction zones. *Earth Planet. Sci. Lett.*  
891 **163**(1-4), 167-174.

892 Morteani G., Möller P., Dulski P. and Preinfalk C. (2014) Major, trace element and stable  
893 isotope composition of water and muds precipitated from the hot springs of Bolivia: Are  
894 the waters of the spring's potential ore forming fluids? *Chemie der Erde-Geochemistry*  
895 **74**(1), 49-62.

896 Nier A. O. (1950) A redetermination of the relative abundances of the isotopes of carbon,  
897 nitrogen, oxygen, argon and potassium. *Phys. Rev.* **77**(6), 789-793.

898 Ozima M. and Podosek F. A. (2002) *Noble Gas Geochemistry*. Cambridge University  
899 Press.

900 Pace A., Bourillot R., Bouton A., Vennin E., Braissant O., Dupraz C., Duteil T.,  
901 Bundeleva I., Patrier P., Galaup S., Yokoyama Y., Franceschi M., Virgone A. and

902 Visscher P.T. (2018) Formation of stromatolite lamina at the interface of oxygenic–  
903 anoxygenic photosynthesis. *Geobiology* **16**(4), 378-398.

904 Parkhurst D.L. and Appelo C.A.J. (2013) Description of input and examples for  
905 PHREEQC version 3 – a computer program for speciation, batch-reaction, one-  
906 dimensional transport, and inverse geochemical calculations. U.S. geological survey  
907 techniques and methods, book 6, chap. A43, pp 497.

908 Pierret M. C., Clauer N., Bosch D., Blanc G. and France-Lanord C. (2001). Chemical and  
909 isotopic ( $^{87}\text{Sr}/^{86}\text{Sr}$ ,  $\delta^{18}\text{O}$ ,  $\delta\text{D}$ ) constraints to the formation processes of Red-Sea brines.  
910 *Geochim. Cosmochim. Acta* **65**(8), 1259-1275.

911 Pin C. and Bassin C. (1992) Evaluation of a strontium-specific extraction  
912 chromatographic method for isotopic analysis in geological materials. *Analytica Chimica*  
913 *Acta* **269**(2), 249-255.

914 Pineau F. and Javoy M. (1983) Carbon isotopes and concentrations in mid-Atlantic ridge  
915 basalts. *Earth Planet. Sci. Lett.* **29**, 413-421.

916 Ray M.C., Hilton D.R., Muñoz J., Fischer T.P. and Shaw A.M. (2009) The effects of  
917 volatile recycling, degassing and crustal contamination on the helium and carbon  
918 geochemistry of hydrothermal fluids from the Southern Volcanic Zone of Chile. *Chem.*  
919 *Geol.* **266**(1-2), 38-49.

920 Risacher F. and Eugster H. P. (1979) Holocene pisoliths and encrustations associated  
921 with spring-fed surface pools, Pastos Grandes, Bolivia. *Sedimentology* **26**(2), 253-270.

922 Risacher F. and Fritz B. (1991) Geochemistry of Bolivian salars, Lipez, southern  
923 Altiplano: origin of solutes and brine evolution. *Geochim. Cosmochim. Acta* **55**(3), 687-  
924 705.

925 Risacher F., and Alonso H. (2001) Geochemistry of ash leachates from the 1993 Lascar  
926 eruption, northern Chile. Implication for recycling of ancient evaporites. *J. volcano.*  
927 *geoth. Res.* **109**(4), 319-337.

928 Risacher F. and Fritz B. (2009) Origin of salts and brine evolution of Bolivian and  
929 Chilean salars. *Aquat. Geochem.* **15**(1-2), 123-157.

930 Risacher F., Alonso H. and Salazar C. (2003) The origin of brines and salts in Chilean  
931 salars: a hydrochemical review. *Earth-Sci. Rev.* **63**(3-4), 249-293.

932 Risacher F., Fritz B. and Hauser A. (2011) Origin of components in Chilean thermal  
933 waters. *J. S. Am. Earth Sci.* **31**(1), 153-170.

934 Rissmann C., Leybourne M., Benn C. and Christenson B. (2015) The origin of solutes  
935 within the groundwaters of a high Andean aquifer. *Chem. Geol.* **396**, 164-181.

936 Roche M.A., Fernandez Jauregui C., Aliaga A., Bourges J., Cortes J., Guyot J.L., Pena J.  
937 and

938 Rosner M., Erzinger J., Franz G. and Trumbull R.B. (2003) Slab- derived boron isotope  
939 signatures in arc volcanic rocks from the Central Andes and evidence for boron isotope  
940 fractionation during progressive slab dehydration. *Geochem. Geophys. Geosy.* **4**, 1–25.

941 Rothstein D.A. and Manning C.E. (2003) Geothermal gradients in continental magmatic  
942 arcs: Constraints from the eastern Peninsular Ranges batholith, Baja California, México.  
943 In *Tectonic evolution of northwestern México and the southwestern USA: Boulder,*  
944 *Colorado* (eds. Johnson S.E. et al.) *Geological Society of America Special Paper* **374**, pp.  
945 337–354.

946 Rouchon V., Courtial X., Durand I., Garcia B., Creon L. and Mougín P. (2016) A Fluid  
947 Phase

948 Equilibria Model in the System CO<sub>2</sub>-N<sub>2</sub>-H<sub>2</sub>O-NaCl-He-Ne-Ar Below 200 Bar and 150°C  
949 – Application to CO<sub>2</sub>/He Fractionation in Continental Mantle Degassing. Goldschmidt  
950 Abstracts 2658.

951 Rounds S. A., and Wilde F. D. (2012) Chapter A6. Section 6.6. Alkalinity and acid  
952 neutralizing capacity. In US Geological Survey TWRI book 09.

953 Ryu J. S., Vigier N., Lee S. W., Lee K. S. and Chadwick O. A. (2014) Variation of  
954 lithium isotope geochemistry during basalt weathering and secondary mineral  
955 transformations in Hawaii. *Geochim. Cosmochim. Acta* **145**, 103-115.

956 Salisbury M. J., Jicha B. R., de Silva S. L., Singer B. S., Jiménez N. C., and Ort M. H.  
957 (2011) <sup>40</sup>Ar/<sup>39</sup>Ar chronostratigraphy of Altiplano-Puna volcanic complex ignimbrites  
958 reveals the development of a major magmatic province. *Bulletin*, 123(5-6), 821-840.

959 Sano Y. and Marty B. (1995) Origin of carbon in fumarolic gas from island arcs. *Chem.*  
960 *Geol.* **119**(1-4), 265-274.

961 Sano Y., Takahata N., Nishio Y. and Marty B. (1998) Nitrogen recycling in subduction  
962 zones. *Geophy. Res. Lett.* **25**, 2289-2292.

963 Santoyo E., and Díaz-González L. (2010) A new improved proposal of the Na/K  
964 geothermometer to estimate deep equilibrium temperatures and their uncertainties in  
965 geothermal systems. Proceedings World Geothermal Congress, Bali, Indonesia.

966 Sanjuan B., Millot R., Ásmundsson R., Brach M. and Giroud N. (2014) Use of two new  
967 Na/Li geothermometric relationships for geothermal fluids in volcanic environments.  
968 *Chem. Geol.* **389**, 60-81.

969 Spiro B., Hoke L. and Chenery C. (1997) Carbon-isotope characteristics of CO<sub>2</sub> and CH<sub>4</sub>  
970 in geothermal springs from the Central Andes. *Internat. Geol. Rev.* **39**(10), 938-947.

971 Springer M., and Förster, A. (1998). Heat-flow density across the central Andean  
972 subduction zone. *Tectonophysics* **291**, 123-139.

973 Teboul P. A., Durllet C., Gaucher E. C., Virgone A., Girard J. P., Curie J., ... and Camoin  
974 G. F. (2016) Origins of elements building travertine and tufa: New perspectives provided  
975 by isotopic and geochemical tracers. *Sedim. Geol.* **334**, 97-114.

976 Teboul P. A. (2017) Diagenesis of lower Cretaceous presalt continental carbonates from  
977 the West African margin: simulations and analogues (Doctoral dissertation, Aix-  
978 Marseille).

979 Terra G.J.S., Spadini A.R., França A.B., Sombra C.L., Zambonato E.E., da Silva  
980 Juschaks L.C., Arienti L.M., Erthal M.M., Blauth M., Franco M.P., Matsuda N.S., da  
981 Silva N.G.C., Moretti Junior P.A., D'Avila R.S.F., de Souza R.S., Tonietto S.N., Couto  
982 dos Anjos S.M., Campinho V.S. and Winter W.R. (2010) Classificação de rochas  
983 carbonáticas aplicável às bacias sedimentares brasileiras. *Bulletin Geoscience Petrobras,*  
984 *Rio de Janeiro* **18** (1), 9–29

985 Thorpe R. S., Potts P. J., and Francis P. W. (1976) Rare earth data and petrogenesis of  
986 andesite from the North Chilean Andes. *Contrib. Mineral. Petr.* **54**(1), 65-78.

987 Tosca N.J., Wright V.P. (2015) Diagenetic pathways linked to labile Mg-clays in  
988 lacustrine carbonate reservoirs: a model for the origin of secondary porosity in the  
989 Cretaceous Pre-salt Barra Velha Formation, Offshore Brazil, 435. *Geological Society of*  
990 *London, Special Publication.* SP435-1.

991 Vengosh A., Kolodny Y., Starinsky A., Chivas A. R. and McCulloch M. T. (1991)  
992 Coprecipitation and isotopic fractionation of boron in modern biogenic carbonates.  
993 *Geochim. Cosmochim. Acta* **55**(10), 2901-2910.

- 994 Verkouteren R. M. and Klinedinst D. B. (2004) Value Assignment and Uncertainty  
995 Estimation of Selected Light Stable Isotope Reference Materials: RMs 8543-8545, RMs  
996 8562-8564, and RM 8566. *NIST Special Publication* **260** (149), 59.
- 997 Verma S. P. and Santoyo E. (1997) New improved equations for Na/K, Na/Li and SiO<sub>2</sub>  
998 geothermometers by outlier detection and rejection. *J. Volcanol. Geoth. Res.* **79**(1-2), 9-  
999 23.
- 1000 Verrecchia E.P. (2007) Lacustrine and palustrine geochemical sediments - Chapter 9. In:  
1001 *Terrestrial geochemical sediments and geomorphology* (Eds. D.J. Nash and S.J.  
1002 McLaren), Blackwell, London, Oxford, pp. 298-329.
- 1003 Zamanian K., Pustovoytov K. and Kuzyakov Y. (2016). Pedogenic carbonates: Forms  
1004 and formation processes. *Earth-Sci. Rev.* **157**, 1-17.



## Figure Captions

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1007 Fig. 1: **a.** Topographic map of the Central Andes showing the location of Laguna Pastos  
1008 Grandes among the main Chilean and Bolivian salars (in white); **b.** Zoom on the geological  
1009 context of Laguna Pastos Grandes (modified from Bougeault et al., 2019); satellite image  
1010 provided by Zoom Earth website, © 2018 Microsoft Corporation Earthstar Geographics  
1011 SIO; **c.** View of the carbonate platform with partially submerged calcitic pisoliths.

1012

1013 Fig. 2: Location of water and gas sampling in streams (blue stars), thermal springs (red  
1014 stars) and brine in one of the sustainable lakes (yellow star) in Laguna Pastos Grandes  
1015 (Bolivia). The location of the volcanic rock samples is also indicated by black dots. The  
1016 four thermal springs (images 1-4) flow up through the recent carbonate platform  
1017 developing to the west of the laguna. The arrows indicate gas bubbling in the water basins,  
1018 except for "El Gigante" where gas and water have separate vents. Ign.: Ignimbrite; Dac.:  
1019 Dacite; And.: Andesite.

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1021 Fig. 3: Relative abundance of air-normalized isotopic composition of noble gas ( $^4\text{He}$ ,  $^{20}\text{Ne}$ ,  
1022  $^{36}\text{Ar}$ ,  $^{40}\text{Ar}/^{36}\text{Ar}$  and  $^3\text{He}/^4\text{He}$ ) in thermal springs El Ojo Verde, La Rumba, La Salsa and El  
1023 Gigante. The normalization values used as references are 295.5 for  $^{40}\text{Ar}/^{36}\text{Ar}$  ratio (Nier,  
1024 1950) and  $1.39 \times 10^{-6}$  for  $^3\text{He}/^4\text{He}$  ratio (Ozima and Podosek, 2002). Helium isotope ratios  
1025 are corrected for the effects of ASW (Air saturated Water) contamination in hydrothermal  
1026 system and are equivalent to  $R_c/R_a$ .

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1028 Fig. 4: Plot of  $\delta^{18}\text{O}$  versus  $\delta^2\text{H}$  for Pastos Grandes waters. Plot b is focused on thermal  
1029 springs (in red) and cold streams (in blue) compared to a rain sample (in white) collected  
1030 at the same altitude during the wet season in March 2017. Two snow samples (grey) were  
1031 also collected during the dry season in January 2016. Rainfall and snow data are presented  
1032 in Table A2. The composition of the lake brine (in yellow) of Pastos Grandes is compared  
1033 to other Andean salars (in black, based on this study and Boschetti et al., 2007; Table A2).  
1034 The Local Meteoric Water Line (LMWL; Chaffaut et al., 1998) and the Local Ground- and  
1035 Spring-Water Line (LGSWL; Rissmann et al., 2015) for the South-Central Andes are also  
1036 indicated.

1037

1038 Fig. 5: Chemical composition of Laguna Pastos Grandes water sources (thermal springs in  
1039 red/orange and streams in blue) and lake brine (in yellow). **a.** Schoeller diagram showing  
1040 relative concentrations in solutes; **b.** Plot of Ca versus Alkalinity (mM); **c.** Plot of Cl  
1041 concentration versus Cl/Br. Data from this study are presented as dots and previous data as  
1042 squares (Ballivian and Risacher, 1981; Hurlbert and Chang, 1984; Risacher and Fritz,  
1043 1991; Jones and Renaut, 1994).

1044

1045 Fig. 6: Sr, Li and B isotopic compositions of Laguna Pastos Grandes water sources (thermal  
1046 springs in red and streams in blue) and lake brine (in yellow) compared with andesite,  
1047 dacite (this study), and rhyolitic ignimbrite (this study and Kaiser, 2014) from the Pastos  
1048 Grandes caldera. **a.**  $^{87}\text{Sr}/^{86}\text{Sr}$  vs Sr concentration (mg/l) data compared to Cenomanian-  
1049 Turonian marine carbonates (McArthur et al., 1994) representing the last marine  
1050 sedimentary sequence in the Central Andes region and modern marine evaporites (Pierret  
1051 et al., 2001). Mean values of dacite (D) and andesite (A) from the Andean Central Volcanic  
1052 Zone (CVZ) are also given for comparison (Cortecci et al., 2005); **b.**  $\delta^{11}\text{B}$  vs  $\delta^7\text{Li}$  data

1053 compared to modern seawater (Boschetti et al., 2017) and rocks from the Andean volcanic  
1054 arc (Chan et al., 2002; Rosner et al., 2003).

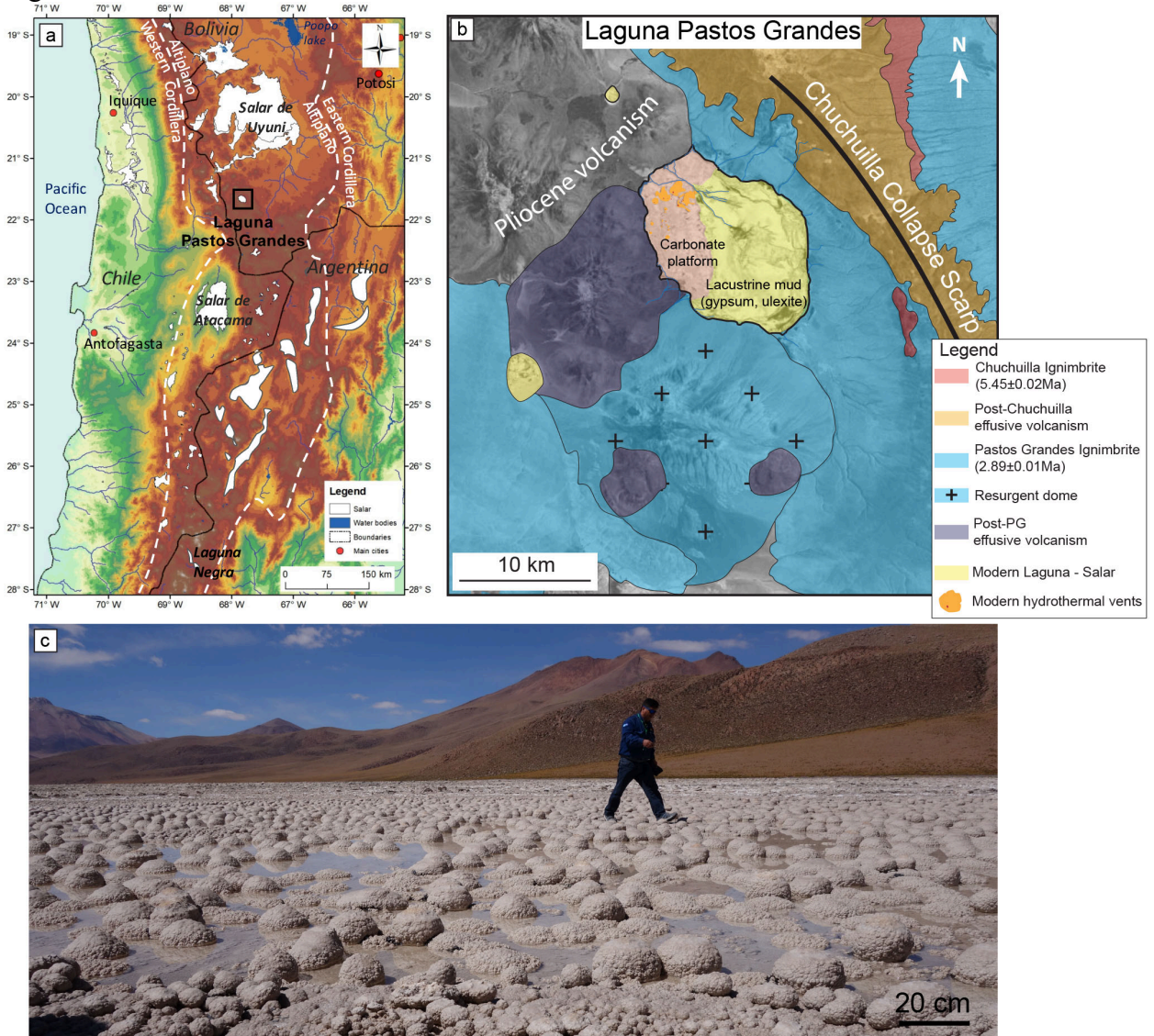
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1056 Fig. 7: Conceptual model of modern carbonate precipitation in relation to water and gas  
1057 sources in Laguna Pastos Grandes. Violet-blue arrows refer to hydrothermal circulations.  
1058 See the conclusion for more details. Boron isotope data are from De Hoog and Savov  
1059 (2018) for the Altered Oceanic Crust (AOC) and marine sediments and Marschall (2018)  
1060 for the mantle. Lithium isotope data are from Chan and Kastner (2000) for subducted  
1061 sediments, Moriguti and Nakamura (1998) and Chan et al. (1992) for AOC and Misra and  
1062 Froelich (2012) for the mantle. Nitrogen isotope data are from Sano et al. (1998) for the  
1063 crust. Carbon isotope data are from Hoefs (1980) for sedimentary organic carbon and  
1064 Pineau and Javoy (1983) for mantle-derived signature. Rc/Ra data are from Hoke et al  
1065 (1994). Other data are from this study.

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Figure 1



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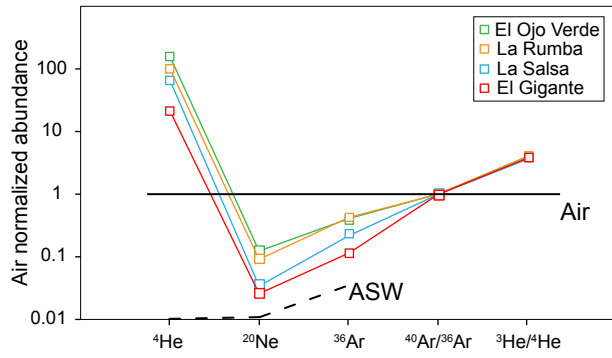
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Figure 2



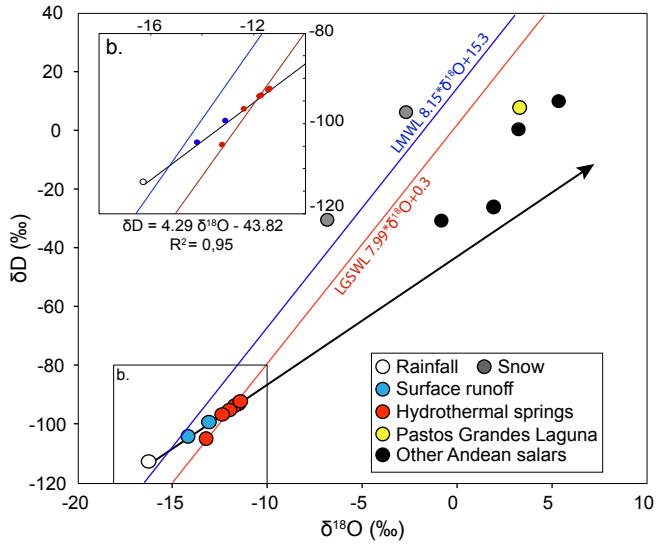
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1073 Figure 3



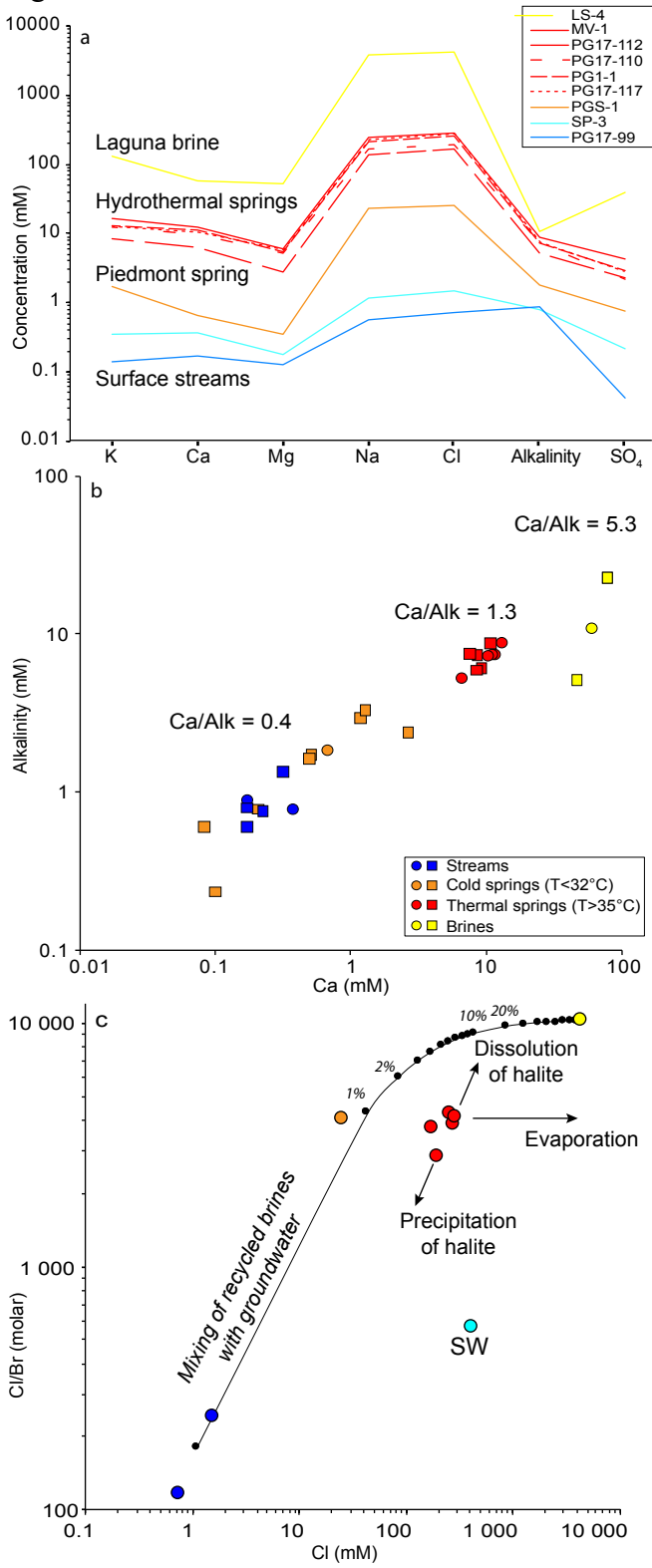
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1076 Figure 4



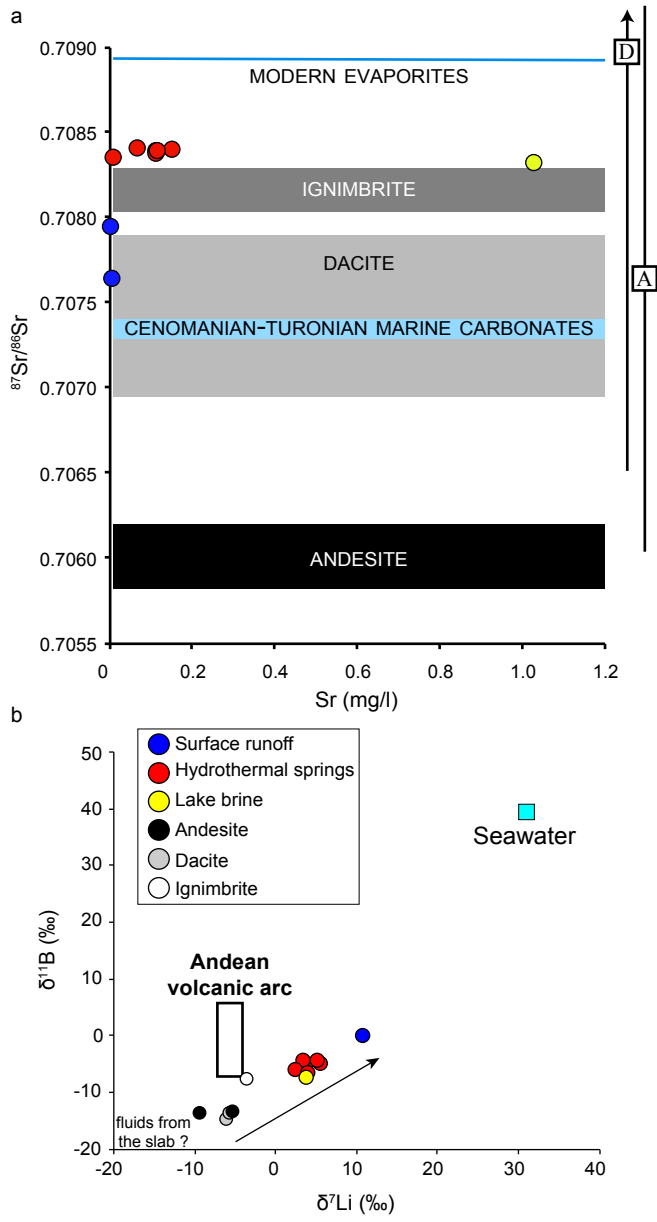
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1079 Figure 5



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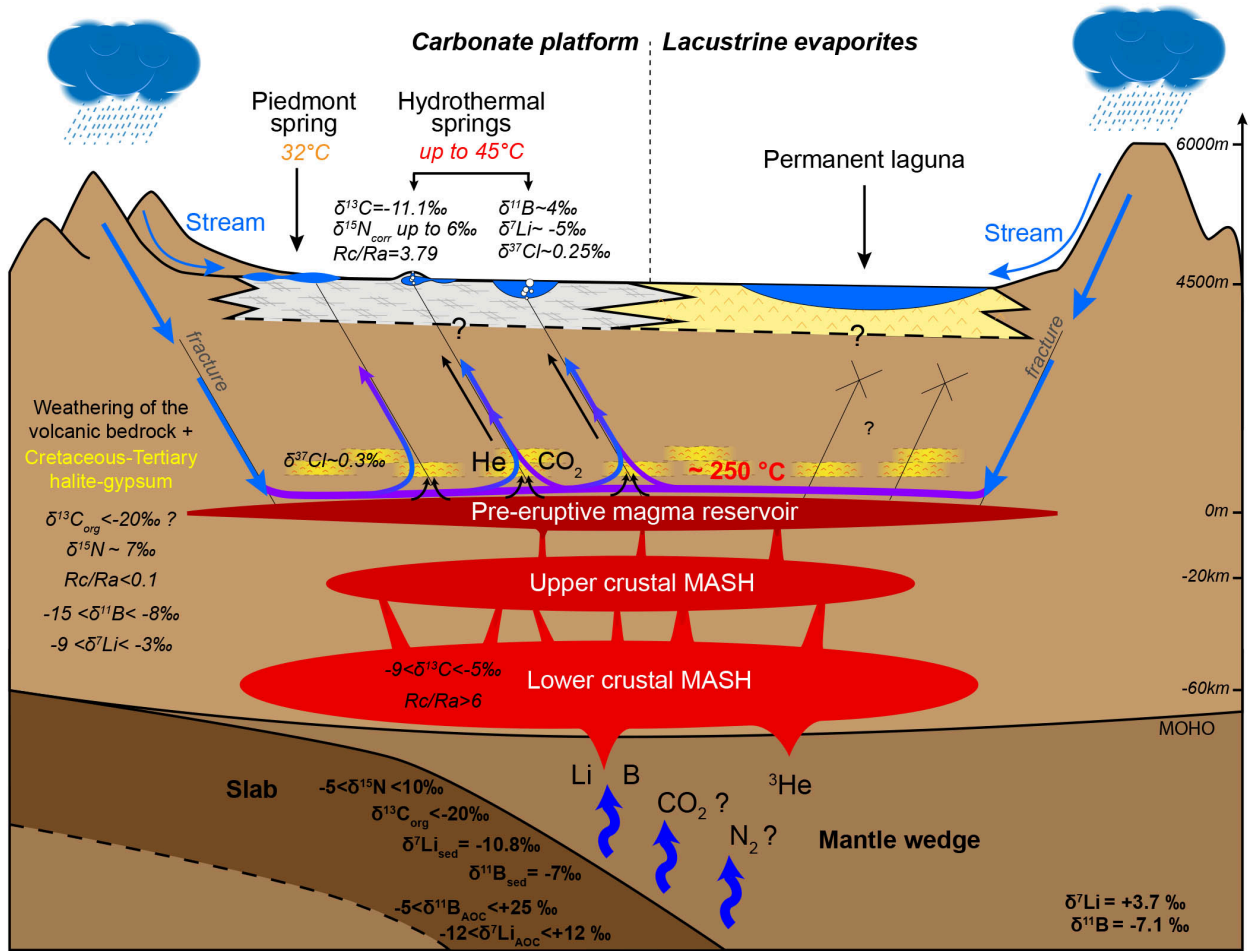
1082 Figure 6



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1085 Figure 7



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Appendix of

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**A Multi-Tracers Analysis of Gas and Solutes in Laguna Pastos Grandes (Bolivia): Key Proxies of the Origin of Continental Carbonates in Andean Salars**

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1101 **Analytical methods**

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**N<sub>2</sub> gas:**  $\delta^{15}\text{N}$  of N<sub>2</sub> gas was measured following the protocol of Li et al. (2009). Purification starts with a cryogenic separation at liquid nitrogen temperature. The non-condensable gases, including N<sub>2</sub>, H<sub>2</sub>, O<sub>2</sub>, CH<sub>4</sub> and He, are inserted in the line and circulated using a mercury Toeppler pump through a CuO reactor maintained at 950 °C for 30 minutes (and then cooled to 450 °C) to oxidize H<sub>2</sub> and CH<sub>4</sub>. The resulting CO<sub>2</sub> and H<sub>2</sub>O are cryogenically trapped at liquid-nitrogen boiling temperature. Excess O<sub>2</sub>, if any, is resorbed and the NO<sub>x</sub> that was potentially generated during the previous oxidation phase is reduced to N<sub>2</sub> by circulating the gases over a Cu reactor maintained at 600 °C. The purified N<sub>2</sub> and He are then collected with the mercury Toeppler pump and manometrically quantified before being transferred in vials for measurement using a dual-inlet IRMS Delta + XP. This instrument is calibrated by measuring an internal reference N<sub>2</sub> gas, itself calibrated against the air, the international reference standard for  $\delta^{15}\text{N}$  measurements, which has by definition an absolute value of  $\delta^{15}\text{N}_{\text{Air}} = 0\text{‰}$ . The CO<sub>2</sub> that was trapped using liquid nitrogen was then released at -140 °C, collected using a liquid N<sub>2</sub> trap and manometrically quantified before being transferred to vials for measurement using the dual-inlet IRMS Delta + XP.  $\delta^{13}\text{C}$  values compare well with those obtained by GC/C/IRMS at the IFPEN laboratory (mean difference < 0.2‰; Table A1).

**Noble gas:** Noble gases were measured following the protocol of Moreira et al. (2018). The gas purification consists of several combustions: the first one with a Bulk Getter (SAES) heating system maintained at 400 °C for 5 minutes, followed by two 5-minute combustions at 800 °C each with titanium sponge. After purification, helium is separated from the other noble gases using activated charcoal at 30 K, introduced into the Helix-SFT mass spectrometer and analyzed using peak jumping. <sup>3</sup>He is collected on the electron multiplier in pulse-counting mode whereas <sup>4</sup>He is analyzed on the Faraday cup and the signal is amplified using either 10<sup>11</sup> ohm or 10<sup>12</sup> ohm resistance depending on the signal. After the helium was measured, neon is released from the cold trap at 70 K. Two

1128 cycles of neon isotope measurement are performed before neon is introduced to stabilize  
1129 the magnet. For each cycle,  $^{20}\text{Ne}$  is measured using a mass-scan instead of setting the  
1130 magnet on the required field to measure  $^{20}\text{Ne}$  (see Moreira et al., 2018 for details).  $^{21}\text{Ne}$ ,  
1131  $^{22}\text{Ne}$ ,  $^{40}\text{Ar}$  and  $\text{CO}_2$  were measured for 10 seconds each using peak switching. Argon is  
1132 partially desorbed at 130 K and transferred to charcoal at the temperature of liquid nitrogen  
1133 for 15 minutes. After the desorption of argon at room temperature from the charcoal trap,  
1134 dilution(s) using a 1 L reservoir is/are used to decrease the amount of argon introduced into  
1135 the mass spectrometer.  $^{36}\text{Ar}$  and  $^{38}\text{Ar}$  are collected on the electron multiplier, whereas  $^{40}\text{Ar}$   
1136 is measured on the Faraday cup using  $10^{11}$  ohm resistance. All the data were corrected  
1137 following the procedure of Moreira et al. (2018).

1138 **B isotopes:**  $\delta^{11}\text{B}$  was measured in rock samples following the protocol of Chetelat  
1139 et al. (2009). Finely powdered sample (50 mg) was admixed with 300 mg of ultra-pure  
1140  $\text{K}_2\text{CO}_3$  in a Pt crucible and melted in a muffle furnace at 950 °C for 15 minutes. The pellet  
1141 was taken up in 3 mL of 0.5  $\text{HNO}_3$  and added to a 50 mL vial filled with 20 mL  $\text{H}_2\text{O}$ . An  
1142 additional 1-2 mL of 0.5N  $\text{HNO}_3$  were added until complete dissolution. The final pH was  
1143 adjusted to pH 1.7 with 3N  $\text{HNO}_3$ , and 7 mL of this solution were passed through 2 mL of  
1144 the cation exchange resin AG 50W-X8 to extract most of the cationic load. The recovered  
1145 solution was adjusted to pH 8-9 with distilled 4N  $\text{NH}_4\text{OH}$  and B was extracted on  
1146 Amberlite IRA-743 resin in two steps: the first step consisted of extraction on a column  
1147 loaded with 300  $\mu\text{L}$  of resin and the second step of purification (after adjustment to pH 8-  
1148 9 again) on a column filled with 50  $\mu\text{L}$  of the resin.  
1149

#### 1150 **Geothermometric calculations**

1151 The silica concentration of our samples is fairly uniform within the range of 101 to 154  
1152 mg/l (Table 2). Applying the quartz geothermometer described in Kharaka and Mariner  
1153 (1989), Verma and Santoyo (1995, 1997) estimated equilibrium temperatures of spring  
1154 water with the rocks of a deep reservoir up to  $163 \pm 3$  °C (assuming no steam loss; Table  
1155 A3) with a mean of  $149 \pm 11$  °C. However, considering the temperature between the surface  
1156 and the deep reservoir, the strong influence of temperature on quartz solubility as well as  
1157 precipitation of silica during water cooling as it ascends to the surface could affect the  
1158 estimated temperature. The Na-K-Ca geothermometer yields similar estimates ( $156 \pm 30$   
1159 °C) when the Mg correction of Fournier and Potter (1979) is applied. But similarly, this  
1160 geothermometer calibrated on silicates can also be affected by a precipitation of silicates  
1161 during the cooling of the thermal water.  
1162

1163 The Na-Li geothermometer gives much higher estimates (around 300 °C) regardless of the  
1164 equation used (Fouillac and Michard, 1981; Kharaka et al., 1982; Verma and Santoyo,  
1165 1993, 1997). Using a larger dataset than in the previous articles, Sanjuan et al. (2014)  
1166 modified the equations of Kharaka et al. (1982) and Fouillac and Michard (1981). Their  
1167 corrections do not modify the results for the Kharaka et al. equation (mean value 325 °C)  
1168 and decrease the values obtained with the Fouillac and Michard equation (mean value 251  
1169 °C) by 50 °C. The Li-Mg geothermometer (Kharaka and Mariner, 1989) yields lower  
1170 values ( $186 \pm 18$  °C; Table A3) than the Na-Li geothermometer. The discrepancies  
1171 observed between the geothermometers using Li can be explained by the high  
1172 concentrations of Li in our samples. The  $\text{Log}(\text{Na}/\text{Li})$  values obtained for the thermal  
1173 springs of Laguna Pastos Grandes are between 1.24 and 1.47 whereas the values used by  
1174 Sanjuan et al. (2014) for their calibrations are never lower than 2.00. Consequently, our

1175 data are not in the range of calibration of the equations and if the correlations cannot be  
1176 extended linearly, the uncertainties on the calculated temperatures will be high.

1177  
1178 The geothermometer based on Li isotopes was also tested as it is independent from the Li  
1179 concentration. This geothermometer was calibrated experimentally on springs from the  
1180 Guadeloupe and Martinique volcanic arcs (Millot et al., 2010). It relies on the fact that Li  
1181 isotopic fractionation ( $\Delta_{\text{solution-solid}}$ ) between solution and basalt is strongly temperature  
1182 dependent with, for example, values of +19.4‰ at 25 °C to 6.7‰ at 250 °C. Considering  
1183 the  $\delta^7\text{Li}$  mean value of  $4.44 \pm 0.90$ ‰ for thermal springs and using the values for rhyolitic  
1184 ignimbrite, dacite and andesite in the area that are reported in Table 3, we obtained a  
1185  $\Delta_{\text{solution-solid}}$  of 8, 10 and 12‰, respectively. Knowing that the Central Andes Ignimbrites  
1186 are a 50:50 mixture of mantle-derived basalts and of regional crust (de Silva and Kay,  
1187 2018), we can hypothesize that the behavior of Li in these rocks and in the altered products  
1188 is not very different from that in the andesite of Guadeloupe. In this case, the calibration  
1189 temperature of Millot et al. (2010) for fractionations between 8 and 12‰ would give a  
1190 temperature of  $200 \pm 25$  °C. The Na-K geothermometer yields similar estimates of  $228 \pm 9$   
1191 °C with the equation of Verma and Santoyo (1997) and  $205 \pm 12$  °C with that of Santoyo  
1192 and Diaz-Gonzalez (2010).

1193

#### 1194 **PHREEQC modeling:**

1195 The mineralogical composition of the volcanic rocks sampled around the Laguna Pastos  
1196 has been determined by DRX as:

- 1197 - Dacite: alkali and potassium feldspar, quartz, biotite
- 1198 - Andesite: alkali feldspar, biotite, olivine, amphibole
- 1199 - Ignimbrite: alkali and potassium feldspar, quartz, biotite, amphibole

1200 As numerous of these minerals are not available in the Thermoddem database, we  
1201 performed the PHREEQC modeling with the selected minerals as follows:

1202 *Solution 1*

1203 *units mmol/l*

1204 *temp 225 # Temperature varying between 200 and 250 °C*

1205 *Equilibrium\_phases 1*

1206 *Quartz(alpha) 0.0 10.0*

1207 *Sanidine 0.0 10.0*

1208 *Albite(low) 0.0 10.0*

1209 *Anorthite 0.0 10.0*

1210 *Pargasite 0.0 10.0*

1211 *Anhydrite 0.0 10.0*

1212 *CO2(g) 1.3 #CO2(g) SI varying between 1-2*

1213 *Halite 0.0 0.239 #Corresponding to the average Cl concentration in*  
1214 *End spring water*

1215

#### 1216 **References**

- 1217 Fouillac C. and Michard G. (1981) Sodium/lithium ratio in water applied to  
1218 geothermometry of geothermal reservoirs. *Geothermics* **10**(1), 55-70.  
1219 Fournier R. O. and Potter Ii R. W. (1979) Magnesium correction to the Na/K/Ca chemical  
1220 geothermometer. *Geochimica et Cosmochimica Acta* **43**(9), 1543-1550.  
1221 Kharaka Y. K., Lico M. S. and Law L. M. (1982) Chemical geothermometers applied to  
1222 formation waters, Gulf of Mexico and California basins. *AAPG Bulletin* **66**(5), 588-588.

1223 Kharaka Y. K. and Mariner R. H. (1989) Chemical geothermometers and their  
1224 application to formation waters from sedimentary basins. In *Thermal history of*  
1225 *sedimentary basins*. Springer, New York, NY. pp. 99-117.  
1226 Verma S. P. and Santoyo E. (1995) New improved equations for Na/K and SiO<sub>2</sub>  
1227 geothermometers by error propagation. *Proc. World Geotherm. Congr 2*, 963-968.  
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1229 **Figure captions**

1230 **Figure A1.** Photography and illustrating schema of bubbling gas sampling method.

1231 **Figure A2.** Comparison of the water composition obtained for the volcanic bedrock  
1232 weathering at 200 (blue), 225 (red) and 250 °C (green) with increasing pCO<sub>2</sub> from 10 bar  
1233 in light color to 100 bar in dark color. The average spring water is in black.

1234 **Figure A3.** Air-normalized helium R/Ra values plotted against He/Ne ratios of gas samples  
1235 from Laguna Pastos Grandes compared with other Andean sources (Hoke et al., 1994).  
1236 Mixing lines between the three main sources of helium (crustal CRUST, mantle MORB  
1237 and air saturated water ASW) are also represented.

1238  
1239 **Figure A4.** Relations between chloride and sodium for Pastos Grandes brines (in yellow)  
1240 and water sources as a function of temperature: thermal spring >35 °C in red, <32 °C in  
1241 orange and cold stream <15 °C in blue. Na-Cl compositions are compared with other  
1242 Bolivian salars (pale triangles; Risacher and Fritz, 1991). Data from this study are reported  
1243 with dots and previous data with squares (Ballivian and Risacher, 1981; Hurlbert and  
1244 Chang, 1984; Risacher and Fritz, 1991; Jones and Renaut, 1994).  
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**Table A1.** Detailed nitrogen and carbon isotopic analysis of gas samples from Laguna Pastos Grandes.

Nitrogen analysis				
Sample	Date	Method	$\delta^{15}\text{N}$ (‰)	1 $\sigma$
PG100	20/07/2017	GC-IRMS on steel tube	2.73	0.03
PG100	20/07/2017	GC-IRMS on steel tube	2.75	0.01
PG112	20/07/2017	GC-IRMS on steel tube	1.79	0.02
PG112	20/07/2017	GC-IRMS on steel tube	1.77	0.01
PG112	07/02/2018	GC-IRMS on exetainer	1.74	0.02
PG116	07/02/2018	GC-IRMS on exetainer	1.60	0.02
PG117	19/07/2017	GC-IRMS on steel tube	2.49	0.05
PG117	19/07/2017	GC-IRMS on steel tube	2.47	0.03
PG117	19/07/2017	GC-IRMS on steel tube	2.24	0.03
PG117	19/07/2017	GC-IRMS on steel tube	2.26	0.02
PG117	19/07/2017	GC-IRMS on steel tube	2.18	0.02
PG117	19/07/2017	GC-IRMS on steel tube	2.17	0.02
Carbon analysis				
Sample	Date	Method	$\delta^{13}\text{C}$ (‰)	1 $\sigma$
PG100	14/06/2017	GC-C-IRMS	-11.36	0.01
PG100	14/06/2017	GC-C-IRMS	-11.32	0.01
PG100	14/06/2017	GC-C-IRMS	-11.31	0.01
PG100	20/07/2017	GC-IRMS	-10.73	0.03
PG100	20/07/2017	GC-IRMS	-11.27	0.03
PG112	14/06/2017	GC-C-IRMS	-11.31	0.01
PG112	14/06/2017	GC-C-IRMS	-11.24	0.01
PG112	14/06/2017	GC-C-IRMS	-11.26	0.01
PG112	20/07/2017	GC-IRMS	-11.11	0.03
PG112	20/07/2017	GC-IRMS	-11.24	0.03
PG116	14/06/2017	GC-C-IRMS	-11.25	0.03
PG116	14/06/2017	GC-C-IRMS	-11.08	0.03
PG116	14/06/2017	GC-C-IRMS	-11.05	0.03
PG116	07/02/2018	GC-IRMS	-11.00	0.04
PG116	07/02/2018	GC-IRMS	-11.49	0.04
PG116	07/02/2018	GC-IRMS	-11.43	0.06
PG117	14/06/2017	GC-C-IRMS	-11.06	0.04
PG117	19/07/2017	GC-IRMS	-10.85	0.05

1248 **Table A2.** Stable isotope compositions of Andean salars water, rainfall and snow from the  
 1249 region of Pastos Grandes (from this study\* and Boschetti et al., 2007).

	$\delta^{18}\text{O}$ ( $\pm 0.1\text{‰}$ , 1s)	$\delta\text{D}$ ( $\pm 0.8\text{‰}$ , 1s)
Chaxa lagoon	-0.8	-30.5
Miñique lagoon	5.4	10.1
Miscanti lagoon	3.3	0.5
Uyuni*	1.9	-26.1
Rainfall*	-16.3	-112.9
Snow 1*	-6.8	-30.3
Snow 2*	-2.7	6.5

1250 **Table A3.** Estimated equilibrium temperatures ( $^{\circ}\text{C}$ ) for hydrothermal sources obtained with  
 1251 different geothermometers.  
 1252

Geothermometer	PG_117	PG_112	PG_100	PG1_1	MV_1	PGS_1	Mean	1s
SiO <sub>2</sub> (Verma and Santoyo, 1997)	145	138	145	163	162	138	149	11
Na/K/Ca – Mg (Fournier and Potter, 1979)	177	144	169	167	171	107	156	26
Na/K (Verma and Santoyo, 1997)	215	226	237	222	230	240	228	9
Na/K (Santoyo and Diaz-Gonzalez, 2010)	188	202	216	197	221	207	205	12
Na/Li (Fouillac and Michard, 1981)	315	316	344	272	283	268	300	30
Na/Li (modified by Sanjuan et al., 2014)	264	264	285	230	239	226	251	23
Na/Li (Verma and Santoyo, 1997)	323	324	351	280	292	276	308	30
Na/Li (Kharaka et al., 1982)	334	335	353	304	312	301	323	21
Na/Li (modified by Sanjuan et al., 2014)	336	337	355	306	314	303	325	21
Mg/Li (Kharaka and Mariner, 1989)	199	193	197	185	192	151	186	18

1253 **Table A4.**  $\delta^{37}\text{Cl}$  analyses of water samples from Laguna Pastos Grandes.

Sample	$\delta^{37}\text{Cl}$ (‰)	1 $\sigma$
La Salsa 1	0.308	0.002
La Salsa 2	0.230	0.010
La Salsa 3	0.230	0.009
La Salsa 4	0.260	0.009
La Salsa 5	0.234	0.003
La Salsa 6	0.292	0.002
La Salsa 7	0.300	0.002
La Rumba 1	0.227	0.010
La Rumba 2	0.205	0.006
La Rumba 3	0.234	0.011
El Ojo Verde 1	0.246	0.009
El Ojo Verde 2	0.252	0.013
<b>Average</b>	<b>0.251</b>	<b>0.032</b>

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1255 **Table A5.** Results of PHREEQC modeling. Alb. Albite(low); Anh. Anhydrite; An. Anorthite;  
 1256 Hal. Halite; Par. Pargasite; Qtz. Quartz(alpha); San. Sanidine

	pCO <sub>2</sub> (bar)	Alb.	Anh.	An.	CO2(g)	Hal.	Par.	Qtz	San.		C	Ca	Cl	K
Input temperature: 200 °C	10	4.9E-2	-5.0E-4	-1.7E-2	-1.0E-1	-2.4E-1	-1.4E-3	-7.6E-2	-1.1E-2	Water chemistry (molality)	1.0E-1	2.0E-2	2.4E-1	1.1E-2
	20	5.0E-2	-5.3E-4	-1.6E-2	-2.0E-1	-2.4E-1	-2.4E-3	-7.6E-2	-1.1E-2		2.0E-1	2.1E-2	2.4E-1	1.1E-2
	40	5.2E-2	-5.7E-4	-1.4E-2	-3.9E-1	-2.4E-1	-4.4E-3	-7.4E-2	-1.1E-2		3.9E-1	2.3E-2	2.4E-1	1.1E-2
	60	5.4E-2	-6.0E-4	-1.2E-2	-5.8E-1	-2.4E-1	-6.3E-3	-7.2E-2	-1.1E-2		5.8E-1	2.5E-2	2.4E-1	1.1E-2
	80	5.5E-2	-6.3E-4	-9.9E-3	-7.6E-1	-2.4E-1	-8.1E-3	-6.9E-2	-1.1E-2		7.6E-1	2.7E-2	2.4E-1	1.1E-2
	100	5.7E-2	-6.6E-4	-7.8E-3	-9.6E-1	-2.4E-1	-1.0E-2	-6.7E-2	-1.1E-2		9.6E-1	2.9E-2	2.4E-1	1.1E-2
Input temperature: 225 °C	10	3.6E-2	-4.5E-4	-9.4E-3	-1.0E-1	-2.4E-1	-6.4E-4	-4.7E-2	-1.5E-2		1.0E-1	1.1E-2	2.4E-1	1.5E-2
	20	3.6E-2	-4.7E-4	-8.9E-3	-2.0E-1	-2.4E-1	-1.1E-3	-4.6E-2	-1.5E-2		2.0E-1	1.2E-2	2.4E-1	1.5E-2
	40	3.7E-2	-4.9E-4	-8.1E-3	-4.0E-1	-2.4E-1	-1.9E-3	-4.5E-2	-1.5E-2		4.0E-1	1.2E-2	2.4E-1	1.5E-2
	60	3.7E-2	-5.1E-4	-7.2E-3	-6.0E-1	-2.4E-1	-2.7E-3	-4.4E-2	-1.5E-2		6.0E-1	1.3E-2	2.4E-1	1.5E-2
	80	3.8E-2	-5.2E-4	-6.3E-3	-7.9E-1	-2.4E-1	-3.4E-3	-4.3E-2	-1.5E-2		7.9E-1	1.4E-2	2.4E-1	1.5E-2
	100	3.8E-2	-5.4E-4	-5.4E-3	-9.9E-1	-2.4E-1	-4.2E-3	-4.1E-2	-1.5E-2		1.0E0	1.4E-2	2.4E-1	1.5E-2
Input temperature: 250 °C	10	3.2E-2	-4.3E-4	-5.8E-3	-1.1E-1	-2.4E-1	-3.0E-4	-3.1E-2	-1.9E-2		1.1E-1	6.8E-3	2.4E-1	1.9E-2
	20	3.2E-2	-4.4E-4	-5.6E-3	-2.2E-1	-2.4E-1	-5.0E-4	-3.1E-2	-1.9E-2		2.2E-1	7.0E-3	2.4E-1	1.9E-2
	40	3.2E-2	-4.5E-4	-5.2E-3	-4.5E-1	-2.4E-1	-8.6E-4	-3.0E-2	-1.9E-2		4.5E-1	7.3E-3	2.4E-1	1.9E-2
	60	3.3E-2	-4.6E-4	-4.8E-3	-6.7E-1	-2.4E-1	-1.2E-3	-3.0E-2	-1.9E-2		6.7E-1	7.6E-3	2.4E-1	1.9E-2
	80	3.3E-2	-4.7E-4	-4.4E-3	-8.8E-1	-2.4E-1	-1.5E-3	-2.9E-2	-1.9E-2		8.9E-1	7.9E-3	2.4E-1	1.9E-2
	100	3.3E-2	-4.7E-4	-4.0E-3	-1.1E0	-2.4E-1	-1.8E-3	-2.9E-2	-1.9E-2		1.1E0	8.2E-3	2.4E-1	1.9E-2

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**Table A6.** Comparison of Laguna Pastos Grandes characteristics with Chilean and Bolivian salars. Data from this study and Hoke et al., 1994; Spiro et al., 1997; Risacher et al., 2003, 2011; Risacher and Fritz, 1991, 2009. ul: ulexite; hal: halite; gyps: gypsum; mirab: mirabilite. \*Previous data TDS: Total Dissolved Solids

	<b>Laguna Pastos Grandes</b>	<b>Chilean salars</b>	<b>Bolivian salars</b>
Location	Bolivian Altiplano	Western Cordillera	Bolivian Altiplano
Basement	Dacite-Andesite- Rhyolitic Ignimbrite	Rhyolitic ignimbrite Andesite	Andesite Rhyodacite
Altitude	4450 m	3400-4300 m	4100-4600 m
Surface	130 km <sup>2</sup>	0.03-400 km <sup>2</sup>	0.03-500 km <sup>2</sup>
Potential evaporation	1400 mm/year	1000-2000 mm/year	1000-1500 mm/year
Precipitation	100 mm/year	40-380 mm/year	50-150 mm/year
Mean temperature	5 °C	0 °C	5-10 °C
Morphology	Playa lake	Mainly playa lakes	Mainly playa lakes
Salinity	256 g/l	1.2-365 g/l	0.4-348 g/l
Brine type ( <i>Na-Cl</i> -)	Ca	65% SO <sub>4</sub> – 24% Ca	52% SO <sub>4</sub> – 26% CO <sub>3</sub> – 19% Ca
Salts	Calcite-gyps.-ul.-hal.	Gyps.-hal.-mirab.-ul.	Gyps.-hal.-mirab.-ul.
Infiltration rate	~negligible	0.01-12.8% of outflow	0.01% - ~inflows
Thermal influence ( <i>T</i> >15°C)	Yes	78 %	60%
Spring T <sub>max</sub>	47 °C (20-75 °C*)	83 °C (Puchuldiza)	36 °C (Challviri)
Spring TDS (range)	14 g/l	3.8 g/l in average (0.2-21.8)	0.82 g/l in average (max. 14)
Mantle influence	47%	69%	44%
CO <sub>2</sub> isotopic composition	-11‰	-8 to -0.6‰	-20 to -6‰

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