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## Surface vitrification caused by natural fires in Late Pleistocene wetlands of the Atacama Desert

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### ► To cite this version:

Pierrick Roperch, Jérôme Gattacceca, Millarca Valenzuela, Bertrand Devouard, Jean-Pierre Lorand, et al.. Surface vitrification caused by natural fires in Late Pleistocene wetlands of the Atacama Desert. *Earth and Planetary Science Letters*, 2017, 469, pp.15-26. 10.1016/j.epsl.2017.04.009 . hal-02889687

**HAL Id: hal-02889687**

**<https://hal.science/hal-02889687v1>**

Submitted on 4 Jul 2020

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1 **Surface vitrification caused by natural fires in Late**  
2 **Pleistocene wetlands of the Atacama Desert**

3

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26 **ABSTRACT**

27 We describe extended occurrences of unusual silicate glass surface layers from the  
28 Atacama Desert (Chile). These glasses, found near the town of Pica at four localities  
29 separated by up to 70 km, are neither fulgurites, nor volcanic glasses, nor metallurgical  
30 slags related to anthropic activity, but show close similarities with other glasses that  
31 have been attributed to large airbursts. <sup>14</sup>C dating and paleomagnetic data indicate that  
32 the glasses were formed during at least two distinct periods, and that they are restricted  
33 to specific Late Pleistocene terrains: paleo-wetlands and soils rich in organic matter  
34 with SiO<sub>2</sub>-rich plant remains, salts and carbonates. This rules out the hypothesis of a  
35 single large airburst as the cause of surface melting. Large oases did indeed form in the  
36 hyperarid Atacama Desert due to elevated groundwater tables and increased surface  
37 discharge during the Central Andean Pluvial Event (roughly coeval with the Mystery  
38 interval and Younger Dryas). Burning of organic-rich soils in dried-out grassy wetlands  
39 during climate oscillations between wet and dry periods rather than a large airburst  
40 explains the formation of the Pica glasses. Finally, we discuss the implications of our  
41 results for other surface glasses previously attributed to extraterrestrial events.

42

43 **Keywords.**

44 Silicate glass, airburst, Wetland, Pyrometamorphism, Younger Dryas, Atacama Desert

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## 50 **1. Introduction**

51 Impact glasses are a common feature associated with many terrestrial impact structures  
52 (French and Koeberl, 2010). Most meteoroids disintegrate during their entry into the  
53 Earth's atmosphere. The Chelyabinsk (Brown et al., 2013) and Tunguska (Svetsov and  
54 Shuvalov, 2008) airbursts were the most recent and best described examples of strong  
55 airbursts but these events were in the low energy range without significant thermal  
56 effects on the ground. Numerical modeling suggests that the energy released by the  
57 largest low-altitude airbursts of cosmic bodies (asteroids, comets) during their entry  
58 into the Earth's atmosphere could be sufficient to produce large catastrophes (Boslough  
59 and Crawford, 2008). Indeed, a large comet airburst has even been proposed to have  
60 caused Younger Dryas cooling (Firestone et al., 2007; Bunch et al., 2012; Wittke et al.,  
61 2013), an explanation that has garnered considerable opposition (see Surovell et al.,  
62 2009; Pigati et al., 2012; Boslough et al., 2013). Melting of the soil surface by radiation  
63 from large aerial burst has also been proposed (Wasson, 2003; Boslough and Crawford,  
64 2008) to explain the formation of some anomalous silicate glasses like the Libyan Desert  
65 Glass (Barrat et al., 1997; Kramers et al., 2013). Other examples include Miocene glass  
66 deposits found in the Argentine pampas (Schultz et al., 2004) as well as Pleistocene  
67 scoriaceous glasses from Australia (Haines et al., 2001) (Edeowie glass, age 0.6 to  
68 0.8Ma) and northern Africa (Osinski et al., 2007; Osinski et al., 2008) (Dakhleh glass, age  
69  $145 \pm 19$  ka). French and Koeberl (2010) point out that it is often difficult to assert an  
70 impact origin to such glasses, which closely resemble non-impact glasses such as  
71 fulgurites, volcanic glasses or even metallurgical slags. The origin and mechanism of  
72 formation of these glasses is thus strongly debated. Hence, proving or disproving the  
73 impact origin of these glasses has implications for estimating the flux of airbursts  
74 producing bolides to the Earth.

75 Massive glass blocks (called Pica Glass, PG) were recently discovered (Blanco and  
76 Tomlinsson, 2013) lying on the surface along the eastern margin of the Tamarugal-  
77 Llamara basin in the Atacama Desert, Chile (Fig. 1). They were interpreted as the  
78 consequence of a major airburst (Blanco and Tomlinsson, 2013). We present field and  
79 petrographic observations, as well as  $^{14}\text{C}$  dating to further constrain their origin.  
80 Paleomagnetism is used here to complement  $^{14}\text{C}$  dating, as it can be used to test the  
81 synchronicity of the glass formation at the different locations. The paleomagnetic study  
82 of the PG and underlying baked clays also constrains the temperature reached by the  
83 clays, and the ambient magnetic field during glass formation. It is also a test for the  
84 origin of the PG as fulgurites. Indeed, lightning strikes create strong magnetic fields (>100  
85 mT) that result in specific remagnetization of the surrounding rocks (Graham, 1961).

86

## 87 **2. Geology and field observations**

88 Dark green, vesiculated (up to 50% vesicles in volume) and irregularly shaped, tabular  
89 glassy bodies occur scattered on the surface at several localities roughly aligned in a  
90 North-South direction and separated by more than 70 km. Here, we will only discuss  
91 observations made at four localities (Puquio de Nuñez, Quebrada Chipana, and  
92 Quebrada Guatacondo, and NW of Pica) (Fig. 1). Individual blocks up to 50 cm wide and  
93 1 to 30 cm thick are scattered over areas up to 1 km<sup>2</sup> in extent (Fig. 2, 3). Their glassy  
94 texture demonstrates high temperature melting and quenching.

95 At Puquio de Nuñez, north of the small oasis of Puquio de Nuñez (Fig. 2a), the glasses are  
96 distributed over a large ~2km<sup>2</sup>, almost flat surface (elevation 1200-1210 m) of late  
97 Pleistocene paleo-wetlands deposits (Blanco and Tomlinsson, 2013; Blanco et al., 2012)  
98 covering a Miocene tectonic flexure on the western border of the basin, which is filled by  
99 Neogene sediments (Nester, 2008). Glass blocks are distributed unevenly and locally

100 concentrated over surfaces up to several tens of meters across (Fig. 2b). Such  
101 concentrations are more frequent on tops of small ridges or ground mounds. Glasses are  
102 also found in the sandy soil covered by a ~10 cm thick layer of sand (Fig. 2e). Some  
103 samples present a striated surface with numerous quartz grains embedded in mm-sized  
104 holes, grooves and tube-shaped cavities that are remnants of plants such as twigs and  
105 roots (Fig. 4; Supplementary Fig. S1).

106 Puquio de Nuñez is presently a very small and mainly artificial (i.e. it has been dug out)  
107 oasis just a few tens of meters wide. Water wells, drilled ~300 m to the east of Puquio de  
108 Nuñez, penetrate the water table located several meters below the present-day arid  
109 surface. A sub-surface fault probably impedes the flow of ground water to the west  
110 bringing it close to the surface in this area. The Puquio de Nuñez area was from time to  
111 time a more humid area in the past (Blanco et al., 2012), when the water table reached  
112 its highest level.

113 At Quebrada de Chipana, located ~35 km south of Puquio de Nuñez, glasses are found in  
114 two separated fields (Fig. 3a). To the west, PG of variable size up to 50 cm thick are  
115 scattered at the surface (Fig. 3b, c). To the east, PG are found directly overlying red clay  
116 sediments that correspond to an old terrace with an overbank clay deposit along the  
117 intermittent stream of Quebrada de Chipana (Fig. 3d, e, f). The clay deposit has been  
118 partly eroded or covered by younger deposits but the best remains can be observed *in*  
119 *situ* with a thickness of about 10 to 30 cm (Fig. 3f). Although erosion has broken up most  
120 of the silicate glasses from the baked clays, we can still find evidence of several glasses  
121 in their *in situ* position just above the clay layer. Silicified plant twigs and imprints are  
122 common in the baked clays (supplementary Fig. S1). A 20-30 cm thick layer of buried  
123 plant material is frequently associated with the glasses (Fig. 4a; supplementary Fig. S1).  
124 Fossil plants, currently composed of silica (50%) and carbonates (20%) with almost no

125 residual organic matter, are often mixed with or underlie the baked clays or the glasses  
126 (Fig. 4c, d; supplementary Fig. S1).

127 At Quebrada Guatacondo, most of the glasses are found north of the Quebrada  
128 (intermittent stream), a few meters above the present-day base level of the stream. The  
129 PG layer is more discontinuous than at the two previous sites (Puquio de Nuñez,  
130 Quebrada de Chipana). Glasses are sometimes found above and below a 10-20 cm thick  
131 white layer composed mainly of burnt but not melted silicified plant remains  
132 (Supplementary Fig. S1). Glasses above the white layer consist mainly of melted silicified  
133 plant twigs. The largest PG blocks, up to 30 cm thick, are found within the soil below the  
134 white layer. Plant remains and plant imprints are also observed in the glasses formed  
135 within the soil (Supplementary Fig. S1c, d).

136 Isolated blocks of PG also occur near and within the town of Pica, but these blocks could  
137 have been transported from their original location. Abundant *in situ* glasses are found  
138 about 9 km to the NW of the town of Pica. The glasses are spread over about 1 km at the  
139 base of the southern and eastern edges of low-lying hills. These hills, related to a  
140 tectonic fault (Blanco et al., 2012; Blanco and Tomlinsson, 2013), limit a paleo-wetland  
141 deposit to the west with a mean elevation of 1100m. Burnt soils without glasses are also  
142 observed on the surface in the same general area.

143 At all localities, most glasses contain plant imprints or silicified plant remains (Fig. 4;  
144 supplementary Fig. S1).

145

### 146 **3. Petrography, mineralogy, geochemistry**

#### 147 *3.1 Samples and Methods*

148 Microscope observations were made on polished thin sections in transmitted light and  
149 reflected light. The samples were then observed with scanning electron microscopes

150 (JEOL JSM 7100F with energy dispersive x-ray spectroscopy (Oxford EDS/EBSD) at  
151 University of Rennes1, and Hitachi S-3000N SEM, at CEREGE, operated at 15 kV, and  
152 fitted with a Bruker X-Flash detector and SPIRIT EDS system).

153 Whole-rock chemical analyses for 13 samples of PG, one sample of silicified plants and  
154 one soil sample were acquired at the Service d'Analyse des Roches et des Minéraux  
155 (CRPG) by ICP-OES for the major elements and ICP-MS for the trace elements and REE.  
156 Sample preparation, analytical conditions, uncertainty and limits of detection are  
157 detailed in Carignan et al. (2001) and in [http://helium.crpq.cnrs-](http://helium.crpq.cnrs-nancy.fr/SARM/pages/roches.html)  
158 [nancy.fr/SARM/pages/roches.html](http://helium.crpq.cnrs-nancy.fr/SARM/pages/roches.html). X-ray fluorescence (XRF) analyses for major and  
159 trace elements were also obtained by the Laboratory of Sernageomin (Chile) in five soil  
160 samples from the Puquío area. Platinum-group elements Ir and Pt were measured in  
161 only one sample with the Nickel Sulphide Fire assay method and ICP-MS finish at  
162 Geosciences Laboratories (Geo Labs, Sudbury, Canada). The elemental composition of  
163 the glass was determined by electron microprobe analysis using a Cameca SX-100 at the  
164 Centre de Microanalyse de Paris VI (CAMPARIS). To avoid loss of the most volatile  
165 elements (Na and Cl in particular), we used a defocused beam of 10  $\mu\text{m}$  diameter, an  
166 accelerating voltage of 15 kV, and a beam current of 4 Na. Eleven samples were analyzed,  
167 with 3 to 7 glass analyses per sample. The chemical data are reported in supplementary  
168 dataset S1.

169 The water content was determined for glassy areas of 1mm in diameter on  $\sim 500 \mu\text{m}$   
170 thick double-polished sections using FTIR transmission microscopy with a VERTEX V70  
171 spectrometer coupled to a Hyperion 3000 infrared microscope (IPAG Grenoble).  
172 Infrared measurement were obtained in the  $4000\text{-}1000 \text{ cm}^{-1}$  spectral range and water  
173 contents were estimated by the intensity of the  $\text{-OH}$  fundamental stretching band at  
174  $3550 \text{ cm}^{-1}$  (using a molar absorptivity coefficient of  $67 \text{ L/mol}$ , Stolper, 1982).



175

176 *3.2 Petrography*

177 The PGs are heterogeneous at the centimeter scale and contain variable amounts of pure  
178 glass (10 to 90%, average 50%) (Fig. 5) mixed with relict mineral grains (quartz,  
179 feldspars, pyroxenes being the most common), and scarce lithic fragments of volcanic  
180 origin. Dendritic crystals of Ca-pyroxene, wollastonite, plagioclase and less frequently  
181 melilite that formed during quenching of the glass are also common (Fig. 5d, e), locally  
182 associated with skeletal crystals of Ti-poor titanomagnetite. Iron sulphide grains  
183 (pyrrhotite or troilite) up to 100  $\mu\text{m}$  are found adjacent to vesicles (Fig. 5b, f, g, h) but  
184 droplets of iron sulphides are also found in the glass (Supplementary Fig. S2). These iron  
185 sulphides, especially those within vesicles, often present a weathering pattern typically  
186 developed in hot desert climate (Supplementary Fig. S2b). Although the ratio of Fe/S  
187 determined by EDS analyses suggests a composition closer to pyrrhotite, their low or  
188 undetected magnetic signals suggest that these particles were antiferromagnetic troilite  
189 (FeS) grains before weathering. Some samples also contain droplets of Ni-free iron  
190 phosphide, generally in association with iron sulphide (Supplementary Fig. S2). EDS  
191 analyses indicate a composition close to  $\text{Fe}_3\text{P}$ . Within some glasses, we observed  
192 numerous droplets of native iron, iron sulphide, and iron phosphide. All sulphide  
193 particles are Ni-free. Rare metallic iron and iron carbides are also found.

194 The PGs contains numerous pyroxene crystallites. Relict grains of quartz within the  
195 silicate glass do not show evidence of melting. A few titanomagnetite grains show  
196 structures suggesting incipient melting and some pyroxene crystals show crystal  
197 overgrowth. Pristine zircon grains indicate that the temperature of decomposition of  
198 zircon to baddeleyite ( $\sim 1775^\circ\text{C}$ , El Goresy, 1965) was never reached.

199 The PGs exhibit several structures that could be interpreted as flow during melting (Fig.  
200 2a). However, these structures are mostly common in samples that display well  
201 organized grooves on the surface and tubes suggesting that the putative flow structure  
202 is related to the melting of silicified plants.

### 203 *3.3 Chemical composition*

204 The bulk compositions of PG are in the range 59-64 wt% SiO<sub>2</sub>, 10-15 wt% Al<sub>2</sub>O<sub>3</sub>, 4-13  
205 wt% Na<sub>2</sub>O, 4.7-6.5 wt% CaO, 3-4.5 wt% Fe<sub>2</sub>O<sub>3</sub> (Supplementary dataset S1). At Puquio de  
206 Nuñez, the sandy soils (dominated by detrital quartz, plagioclase, K-feldspar, Ca-  
207 pyroxene, with accessory zircon, ilmenite, and titanomagnetite) present a slightly more  
208 elevated content of SiO<sub>2</sub> about 66 wt% than the PG. PG samples are enriched in either  
209 Na<sub>2</sub>O or CaO with respect to the sandy soils. Regarding minor elements, the PGs are  
210 clearly depleted, for example in Zr, Pb and Ni compared to the soils. Sr concentrations  
211 are similar in soils and glasses (Supplementary Fig. S3 and supplementary dataset S1).  
212 Electron microprobe analyses of pure glass from all localities show an average  
213 composition similar to that of the whole rock Pica Glass samples (that also contains a  
214 significant and variable fraction of unmelted material), but significant inter-sample  
215 variations are observed: SiO<sub>2</sub> ranges from 58.5 to 70.7 wt%, and Al<sub>2</sub>O<sub>3</sub> from 5.2 to 25.5  
216 wt% Cl from 0.1 to 2.9 wt%. Bulk siderophile transition element contents are low (Ni <  
217 20 ppm, Co < 12 ppm, Cu < 54 ppm) (Supplementary Fig. S3). The search for highly  
218 siderophile element enrichments (platinum-group elements) was unsuccessful (Ir <0.02  
219 ppb; Pt <0.20 ppb). The water content in the glass was determined for 9 samples with 4  
220 to 7 independent measurements. H<sub>2</sub>O content is low (< average of 0.298 wt % ± 0.197)  
221 in all samples but one showing a large spread in 7 individual measurements from 0.160  
222 wt% to 2.6 wt % (Table S1). The bulk composition of the silicified plants is at nearly 50  
223 wt% SiO<sub>2</sub> and CaO 19 wt% (not corrected for the large loss on ignition due to the

224 presence of CO<sub>2</sub> and H<sub>2</sub>O) with a notable total S content of 5.2%. SEM observations,  
225 however, suggest some late deposition of gypsum and calcium carbonates after the  
226 plants were silicified and burnt. The plants are depleted in most minor and trace  
227 elements except Sr compared to sands.

228

#### 229 **4. <sup>14</sup>C dating**

230 We obtained <sup>14</sup>C ages from 11 samples of charcoal and organic matter from plant  
231 remains within the soils containing the PGs (Dataset S2). These ages, and those  
232 previously published (Blanco and Tomlinsson, 2013) for the PG-bearing areas (Table 1),  
233 correspond to the Pleistocene–Holocene transition (Fig. 6). A similar distribution of <sup>14</sup>C  
234 ages was also reported (Nester et al., 2007; Gayo et al., 2012) for nearby locations to the  
235 south of our study area, which was interpreted as evidence for repeated expansions of  
236 riparian/wetland ecosystems, and perennial rivers along the southernmost Pampa del  
237 Tamarugal basin from 17.6–14.2 ka, 12.1–11.4 ka and from 1.01–0.71 ka (Gayo et al.,  
238 2012) (Supplementary Fig. S4).

239 All samples from the Puquio de Nuñez area display younger <sup>14</sup>C ages than those  
240 observed at Quebrada de Chipana (Fig. 6). The two youngest ages were obtained on non-  
241 carbonized roots cutting the layer with carbonized plants, thus providing an upper limit  
242 for the age of the thermal event. The older <sup>14</sup>C ages at Quebrada de Chipana can indicate  
243 either that the thermal event at Quebrada de Chipana is significantly older than the one  
244 at Puquio de Nuñez or that the <sup>14</sup>C ages at Quebrada de Chipana represent ages of  
245 organic matter accumulated on the soil surface at least 2000 years prior to the thermal  
246 event.

247 Taking into account the extremely good preservation of organic matter in the Atacama  
248 Desert, these <sup>14</sup>C ages can only provide a maximum age of the thermal event.

249

## 250 **5. Paleomagnetism**

### 251 *5.1 Paleomagnetic Sampling and Methods*

252 At Puquio de Nuñez, standard 2.5 cm cores were drilled from unoriented blocks of PG. In  
253 blocks with an approximately flat surface, cores were drilled orthogonally to this surface  
254 interpreted as paleohorizontal at the time of PG formation. Fifteen glass samples, found  
255 in the soil covered by a layer of sand in a position suggesting little or no displacement  
256 after emplacement (Fig. 2e), were oriented with a molded horizontal plaster cap.

257 At Quebrada de Chipana, eight large blocks of 10 to 20 cm thick baked clays and three  
258 PG blocks were oriented with a plaster cap. In addition, cores were drilled in 20 PG  
259 blocks for which field observations suggested that these were practically *in situ* since the  
260 time of formation. The samples were oriented with magnetic and sun compasses.  
261 Samples from the red clays were then consolidated in the laboratory with sodium  
262 silicate prior to further sub-sampling of standard one-inch diameter cores. Up to six  
263 cores were drilled in each block. We also took several pieces of unoriented fragments of  
264 the fine baked clay beds.

265 The remanent magnetizations were measured at Géosciences Rennes Laboratory with a  
266 2G SQUID magnetometer and demagnetized thermally in a MMTD furnace or by  
267 alternating field (AF) with the 2G online degausser. Thermomagnetic measurements  
268 were performed with the Agico susceptibility meter KLY3 equipped with a CS3 furnace.  
269 Hysteresis data were obtained on 1 to 3 mg whole rock samples with the AGM  
270 magnetometer at LSCE (Gif/Yvette, France). First order reversal curve (FORC) diagrams  
271 were processed with the FORCINEL software (Harrison and Feinberg, 2008).

272 Determination of the paleointensity of the Earth's magnetic field was attempted on 11 of  
273 the baked clay samples and on 85 PG samples using the original Thellier and Thellier

274 (Thellier and Thellier, 1959; Chauvin et al., 2005) or the IZZI (Tauxe and Staudigel,  
275 2004) procedure. For thermoremanent magnetization (TRM) acquisition, the samples  
276 were heated and cooled in air or in vacuum ( $<10^{-2}$  mbar) under an applied dc field  
277 (Dataset S3) ranging from 30 to 50  $\mu$ T. Experiments were performed either on whole  
278 cores or on small fragments of unoriented samples that were fixed in a quartz tube using  
279 non-magnetic glass fibers and sodium silicate. A partial TRM check was performed every  
280 two temperature steps to check for heating induced mineralogical changes.

281 Archeomagnetic studies on bricks and ceramics have often shown a strong anisotropy of  
282 TRM. Thus, the magnetic anisotropy of the baked clays was determined with TRM  
283 acquisition in six positions (+x,-x,+y,-y,+z,-z). The cooling rate effect (Yu, 2011) on  
284 paleointensity determinations was tested only on the baked clays using a linear cooling  
285 rate of 0.3  $^{\circ}$ C/mn compared to the fastest cooling rate ( $>10$   $^{\circ}$ C/mn) used for the routine  
286 paleointensity experiments.

## 287 *5.2 Magnetic properties*

288 Baked clay samples (Quebrada de Chipana) have the highest magnetic susceptibility and  
289 natural remanent magnetization (NRM) while the magnetic properties of the glasses at  
290 Puquio de Nuñez differ clearly from those at Quebrada de Chipana (Fig. 7).

291 PG samples with a large amount of glass at Puquio de Nuñez have the lowest NRM. The  
292 highest magnetic content of PG samples at Quebrada de Chipana is related to the highest  
293 content in relict grains and magnetite crystallites in the glass matrix. Samples from  
294 Quebrada de Guatacondo have a wide range of magnetic properties overlapping those of  
295 the Puquio de Nuñez and Quebrada de Chipana fields.

296 All samples of baked clays and silicate glasses record stable univectorial characteristic  
297 remanent magnetizations (ChRMs). Silicate glasses have a high stability upon AF

298 demagnetization with high medium destructive field values, allowing us to dismiss a  
299 possible lightning effect (Fig. 7).

300 The baked clays have two magnetic phases, one being magnetite and a higher coercivity  
301 phase carrying from 10 to 60% of the remanent magnetization not demagnetized above  
302 100 mT (Fig. 7). The two phases are also recognized in hysteresis data (Fig. S5). This  
303 behavior is often observed in archeomagnetic studies on bricks. The high coercivity  
304 phase is common in bricks fired at high temperatures, and is likely due to the  
305 transformation of iron-rich clays at high temperatures. Distributed unblocking  
306 temperatures in the range 200-550°C is also a characteristic of archeomagnetic  
307 materials (Chauvin et al., 2000; McIntosh et al., 2011). We can conclude, therefore, that  
308 the baked soils in the present study have likely reached temperatures similar to those  
309 used to form archeological bricks (~700°C or above).

310 All glass samples show hysteresis cycles characteristic of magnetite, except one with  
311 saturation above 0.5T indicating a possible contribution from metallic iron  
312 (Supplementary Fig. S5). No evidence of pyrrhotite was found in thermomagnetic  
313 experiments. Further work is needed to decipher the contribution of iron sulphides to  
314 the magnetic signal.

### 315 *5.3 Paleomagnetic directions*

316 The baked clays at Quebrada de Chipana record well-clustered characteristic remanent  
317 magnetization (ChRM) directions (Fig. 8), except for one sample probably taken on a  
318 more disrupted part of the baked clay.

319 The direction of the PG at Quebrada de Chipana present some scatter because the blocks  
320 have likely been slightly disturbed since their formation but the mean ChRM direction  
321 determined from the glasses is indistinguishable from the one recorded by the baked  
322 clays (Table 2, Fig. 8).

323 ChRMs were determined for fifteen oriented samples at Puquio de Nuñez. The mean  
324 paleomagnetic direction recorded by the PG at Puquio de Nuñez is statistically different  
325 from the mean direction recorded by the baked clays or the PG at Quebrada de Chipana  
326 (Fig. 8). In order to further constrain the paleomagnetic test, we also determined the  
327 ChRM directions obtained from cores drilled perpendicular to nearly flat PG surface in  
328 61 non oriented blocks found lying at the surface. Nine samples have a positive  
329 inclination at more than  $45^\circ$  from the mean direction. The mean inclination (angle to the  
330 surface) determined from the 52 unoriented blocks is  $-21.8^\circ$  with an angle of confidence  
331 at 95% of  $7.2^\circ$  (Table 2). The nine samples yielding high positive inclinations were  
332 interpreted as overturned samples. If we invert the inclination for these samples, the  
333 mean inclination for the 61 samples is  $-24.8^\circ \pm 6.7^\circ$ . This mean inclination determined in  
334 the unoriented PG samples is in agreement with the inclination recorded by the oriented  
335 PG blocks.

336 At Quebrada de Guatacondo, the number of oriented cores is too low for a statistical  
337 comparison with the paleomagnetic result in the baked clays at Quebrada de Chipana.

#### 338 *5.4 Paleointensity experiments*

339 Paleointensity determinations were attempted on 96 samples and 70 samples provided  
340 results with acceptable quality (Fig. 7, supplementary Fig. S6, Dataset S3). This high  
341 success rate is due to a NRM carried mainly by single domain grains of magnetite. The  
342 quality factor  $q$  is greater than 29 for more than 50% of the samples. PG samples with  
343 optical evidence of iron sulphides in the vesicles were the most affected by alteration  
344 during heating. This was easily characterized by the acquisition of a Chemical Remanent  
345 Magnetization in the direction of the applied field during the first step of the  
346 paleointensity experiment above  $\sim 300^\circ\text{C}$  (Supplementary Fig. S6).

347

348 The baked clays provide very high quality paleointensity results with quality factors up  
349 to 150. The magnetic anisotropy correction is low. A cooling rate effect of 5 to 7% was  
350 observed in all samples except sample 13PI\_P10a. These results are typical of those  
351 observed in archeological studies on bricks (Chauvin et al., 2000). It is difficult to  
352 estimate the natural cooling rate but cooling below 200°C is likely to occur within hours  
353 taking into account the thickness of the baked layer (20-40 cm). Thus the initial cooling  
354 rate is likely near the slowest cooling rate used in the laboratory.

355 The baked clays at Quebrada de Chipana give a well-defined paleointensity of  $39.4 \pm 1.6$   
356  $\mu\text{T}$  after correction for anisotropy and cooling rate. The mean value from 18  
357 determinations on PG samples from the Quebrada de Chipana locality is similar to the  
358 mean paleointensity determined for the baked clays (Fig. 8, Table 2).

359 The determination of the paleointensity was successful in 36 specimens at Puquio de  
360 Nuñez and most samples from the Puquio de Nuñez area provide significantly lower  
361 paleointensities than those observed in the baked clay samples of Quebrada Chipana  
362 (Fig. 8). Two groups of paleointensity values are observed. Twenty six determinations  
363 from 25 independent PG blocks provide a low field value of  $20.9 \pm 1.2 \mu\text{T}$ . The other  
364 group of 10 determinations, but from only three different blocks, provides a mean  
365 paleointensity value similar to the one at Quebrada de Chipana and at Quebrada de  
366 Guatacondo (Table 2).

367 The paleomagnetic directions and the paleointensity results are statistically different at  
368 Puquio de Nuñez and Quebrada de Chipana which are only separated by a few tens of  
369 km. This observation demonstrates that the thermal events at Puquio de Nuñez and  
370 Quebrada de Chipana did not occur under the same geomagnetic field configuration. The  
371 differences between the ChRM directions ( $\sim 20^\circ$ ) and paleointensity results ( $\sim 20\mu\text{T}$ ) at  
372 Puquio de Nuñez and Quebrada de Chipana are large enough to indicate the record of a



373 significant secular variation of the Earth's magnetic field. Such variations in inclination  
374 and intensity are only reasonable over a few centuries. For instance, such variations  
375 have occurred in Chile over the last three centuries (Roperch et al., 2015) that are  
376 characterized by very high rate of variations in magnetic inclination (up to  $0.12^\circ/\text{yr}$ ) and  
377 in field intensity (up to  $0.15\mu\text{T}/\text{yr}$ ). Altogether, the paleomagnetic data prove that the  
378 glasses at Quebrada Chipana and Puquio de Nuñez were formed at different times  
379 separated by at least a few hundred years.

#### 380 *5.6 Paleomagnetic test of a thermal event away from the glass fields*

381 If the silicate glasses were formed during an airburst, evidence of thermal heating at  
382 high temperature should also be found elsewhere, i.e. away from the glass fields. About  
383 200 m north of the Quebrada Chipana, at an elevation about 50 m above the silicate  
384 glass field, there is a meseta without glasses but with clasts of silicified limestone at the  
385 surface (Fig 3a). In view of the extremely low erosion rates in the Atacama Desert since  
386 the Miocene (Dunai et al., 2005), these clasts were likely already on the surface at the  
387 time of the formation of the PGs. We collected 15 unoriented clasts with sizes around 5  
388 cm to test the hypothesis of a partial thermal remagnetization event. The samples were  
389 demagnetized in zero field and remagnetized in a field of  $40\mu\text{T}$  as in the paleointensity  
390 experiments. The TRM acquired in the laboratory at  $460^\circ\text{C}$  are up to 10 times the  
391 intensity of the NRM. There is no paleomagnetic evidence for any thermal event having  
392 affected the clasts. Moreover, most samples showed profound color changes during  
393 heating above  $400^\circ\text{C}$ , indicating that they were not heated above this temperature since  
394 their formation. Overall, these experiments indicate that this surface, located only 200 m  
395 away from the glass fields, was never heated significantly.

396

## 397 **6. Discussion**

398 The areal extent of the Pica Glass and their composition are unlike any known historical  
399 or prehistorical metallurgy slag deposit, precluding an anthropogenic origin. The  
400 location (70 km west of the closest volcanic arc), the shape and size of the blocks, and  
401 the mineralogy are inconsistent with a volcanic origin.

402 Glassy rocks, called fulgurites, can be formed in the subsoil by lightning in the form of  
403 hollow tubes (Sponholz et al., 1993; Pasek et al., 2012). They are usually 1-2 cm in  
404 diameter, with millimeter thick walls, but can in exceptional circumstances extends to  
405 several meters depth and attain diameters of up to 15 cm. These characteristics strongly  
406 contrast with the large areal distribution of the PG and with the occurrence of baked  
407 soils over an area of 0.1 km<sup>2</sup>. Heating of this thick baked layer or the formation of glasses  
408 by lightning would imply an unrealistic number of lightning strikes on the same surface.  
409 Moreover none of the PG and associated baked clay samples shows remagnetization by  
410 strong fields (Fig. 7), which would be expected in case of successive adjacent lightning  
411 strikes.

412 Another possible formation mechanism for surface glasses is a hypervelocity impact  
413 (French and Koeberl, 2010). The PGs cannot be distal impact ejecta deposits because  
414 such ejecta could not produce a 20 cm-thick layer of baked clays. We found no  
415 geochemical evidence for contamination by an impacting body, with no enrichment in  
416 metallic or platinoid elements in the glass. Textural evidence shows that iron sulphide  
417 droplets were formed in situ mostly on the walls of gas vesicles (Fig. 5, Fig. S2).

418 The large spread of <sup>14</sup>C ages and the different paleomagnetic fields (direction and  
419 intensity) between localities Puquio de Nuñez and Quebrada de Chipana show that the  
420 glasses were not formed synchronously at these sites, and thus cannot have formed  
421 during a single thermal event triggered by a large airburst. Just as important is that we  
422 were unable to find any evidence for a surface thermal event on the mesas immediately

423 adjacent to the specific low-elevation areas where glasses are found at Quebrada de  
424 Chipana.

425 The only remaining viable hypothesis to account for the formation of PGs is akin to  
426 pyrometamorphism during coal fires (Grapes, 2011; Stracher et al., 2011) or methane  
427 flares forming paralavas (Grapes et al., 2013). The grooves on the surface of PG blocks  
428 and tube-shape cavities found in many samples are remnants of melted silicified plants  
429 and twigs. These plant remnants and imprints indicate that vegetation played a pivotal  
430 role in the formation of the glasses. Cases of glass formation during fires of phytolith-  
431 rich plants have been reported (Vélain, 1878; Baker and Baker, 1963). Vélain (1878)  
432 made the first petrographic description of glasses found within ashes after haystack  
433 fires in France. He clearly related the chemical composition of the glasses to the nature  
434 and type of the burned hay or wheat, and pointed out that the extraterrestrial origin,  
435 popularly attributed to these unusual glasses in the 19<sup>th</sup> century, was only the result of  
436 superstition. Baker and Baker (1963) also made a detailed description of silica glass  
437 formation during the burning of two large haystacks in Australia. Fusion and melting of  
438 the opal phytoliths contained in the ~325 tons of pasture plants yielded about 16 tons of  
439 silica glass (Baker and Baker, 1963).

440 The <sup>14</sup>C ages of the plant remains further correlate with the timing of the two phases of  
441 the Central Andean Pluvial Event (CAPE) (Fig. S5), a multi-millennial scale event of  
442 increased rainfall in the high Andes (Quade et al., 2008), which are roughly coeval with  
443 the two major periods of sea surface temperature drops in the north Atlantic (the so-  
444 called Mystery Interval and the Younger Dryas) (Broecker et al., 2010). These two  
445 periods also correspond for the most part to the maximum highstands of paleolake  
446 Tauca nearly 100 m above the present-day surface of salars of Uyuni and Coipasa that  
447 cover a large area of the southern Bolivian Altiplano (Fig. 1) (Sylvestre et al., 1999;

448 Plackzek et al., 2006; Blard et al., 2009; Gayo et al., 2012; Quesada et al., 2015). As  
449 precipitation in the high Andes increased discharge and elevated groundwater tables  
450 (Quade et al., 2008), large oases formed throughout the western Andean piedmont  
451 across the Atacama Desert (Rech et al., 2002, 2003, Saez et al., 2016). The present-day  
452 distribution of the glasses at Puquío de Nuñez roughly corresponds to an extensive  
453 paleowetland extending more than 3 km to the north of the present-day Puquío de  
454 Nuñez small oasis. Except for brief interludes of increased groundwater tables (2.5 – 1.7,  
455 1.01 – 0.71 ka) most of the Holocene has been hyperarid in the Atacama (Gayo et al.,  
456 2012).

457 We thus propose that the PGs were produced *in situ* by fires in dry wetland soils rich in  
458 organic matter and siliceous plant remains (Pigati et al., 2014). Microscopic  
459 observations in thin section of apparent flow structures in samples displaying surface  
460 grooves suggest that the structures are likely remnants of melted elongated silicified  
461 plant materials. The water content in the glass is low (average of 0.298 wt %  $\pm$  0.197,  
462 Table S1), but above the range of most impact glasses (Beran and Koeberl, 1997). Beran  
463 and Koeberl (1997) suggest that only very low H<sub>2</sub>O contents in glasses (< 0.05 wt%) are  
464 diagnostic of an origin by impact. Microprobe analyses indicate high Cl values (up to  
465 2.87 wt%) which have also been described from paralavas (Grapes et al., 2013). In some  
466 samples, the silicified remains were not always fully melted during burning of the  
467 organic matter.

468 The PG samples contain detrital relict grains within the glass and the whole-rock  
469 chemical composition of such glasses is intermediate between those of the desert sandy  
470 soil and the silicified plants. Soils with abundant organic matters and SiO<sub>2</sub>-rich  
471 phytoliths, clay minerals and salts (sodium chloride, sodium and calcium sulfates,

472 carbonates, possible nitrates) may have melted at lower temperatures than needed to  
473 melt detrital quartz grains.

474 Temperatures reached during natural fires are usually low at the soil surface (Stoof et al.,  
475 2013) but may rapidly increase in cases of underground burning inside an organic  
476 matter-rich layer beneath a sand lid as in the case of smoldering combustion during peat  
477 fires (Rein et al., 2008). Very few examples of natural subsurface combustion leading to  
478 soil fusion have been reported. Monod and Palausi (1961) first reported evidence of  
479 melted rocks near Lake Faguibine (Mali) but this observation was later mistakenly  
480 interpreted as incipient volcanism (El Abbas et al., 1993). However, Svensen et al.  
481 (2003) demonstrated that subsurface combustion is the cause of heat and soil melting  
482 and these authors suggest that the surface combustion in the Timbuktu region today  
483 could be a frequent phenomenon in northern West Africa. Our observations at Pica  
484 suggest that such fires, especially when very dry conditions facilitated the propagation  
485 of the smoldering front (Prat-Guitart et al., 2016), may account for the formation of  
486 similar irregular slag-like glassy rocks previously attributed to melting of surface  
487 sediments during airbursts (Haines et al., 2001; Schultz et al., 2004; Osinski et al., 2008).  
488 Indeed, the airburst hypothesis for the formation of surface glass mainly relies mostly  
489 on numerical simulations (Wasson, 2003; Shuvalov and Trubetskaya, 2007; Boslough  
490 and Crawford, 2008). As an example, the Dakhleh glass has been attributed to an  
491 airburst (Osinski et al., 2008, Osinski et al., 2007) but evidence for this is sketchy  
492 (Reimold and Koeberl, 2014). The Dakhleh glass shares numerous characteristics with  
493 the PG. In particular they are confined around oases and show abundant imprints of  
494 plants. The similar paleoenvironment at Pica and Dakhleh suggests that specific  
495 paleogeographic conditions may be necessary to form this type of glasses. The  
496 interpretation proposed for the Pica Glass may apply to the Dakhleh glass as well.

497 Similarly, several glass levels with morphological biosignatures such as phytoliths have  
498 been reported from Argentine Pampean glasses (Schultz et al., 2014) and interpreted as  
499 evidence for seven successive local impact events since the late Miocene. We suggest  
500 that these glasses may have also formed by successive *in situ* fires.

501 We propose that melting of soils and silica-rich plants during the burning of organic  
502 matter-rich layers does not require an external event like an airburst but could be  
503 caused by natural fires under specific paleoenvironmental conditions, such as strong  
504 climatic oscillations in arid regions. Self-ignition due to exothermal microbial  
505 decomposition has been proposed for other examples of peat-fires (Chateauneuf et al.,  
506 1986; Svensen et al., 2003) but humans could also have triggered these fires, and a late  
507 Pleistocene archaeological site (ca. 13-11 ka) is also known in the area (Latorre et al.,  
508 2013).

509 The two distinct periods of formation of the PGs refute any link with a single global  
510 worldwide catastrophic impact event, such as the one suggested to have triggered  
511 climate change at the onset of the Younger Dryas (Firestone et al., 2007; Bunch et al.,  
512 2012; and Wittke et al., 2013), a theory that is strongly debated (e.g., Pigati et al., 2012;  
513 Boslough et al., 2013; Holliday et al., 2014; Meltzer et al., 2014; van Hoesel et al., 2014).

514 The complex mineralogical assemblage found in the PG further demonstrates that the  
515 presence of iron sulphides, spherules of magnetite, iron droplets or iron phosphides do  
516 not necessarily indicate an impact event, as fire in a subsurface layer rich in organic  
517 matter may result in the formation of such exotic minerals by reduction of sulfates and  
518 iron oxides.

519

520 **7. Conclusions**

521  $^{14}\text{C}$  dating and paleomagnetism demonstrate that the studied silicate surface glasses  
522 from the Atacama Desert were formed at the end of the Pleistocene during at least two  
523 different thermal events separated by at least several hundred years.

524 The glasses are distributed across the surface of paleowetlands deposits. Melting of  
525  $\text{SiO}_2$ -rich phytoliths and partially silicified plants was an important factor in the  
526 formation of these glasses. Extensive wetlands developed in the Atacama Desert during  
527 the latest Pleistocene due to an elevated groundwater table associated with the CAPE  
528 (an multi-millennial wet event roughly coeval with the Mystery interval and Younger  
529 Dryas) and the maximum highstands of paleolake Tauca in the Bolivian Altiplano.  
530 Organic matter accumulated from grasses and sedges in soils during these wet periods  
531 and subsequent dry periods triggered fires and smoldering combustion in the soil and  
532 plant litter with a very low moisture content. The strong climate oscillations during the  
533 Late Pleistocene would have provided such conditions for near-surface vitrification by  
534 fire.

535 Our results provide clues for revisiting other documented cases of unusual silicate  
536 glasses that in the past have been attributed to airbursts with implications for the  
537 determination of the rate of occurrence of such events on Earth (Boslough and Crawford,  
538 2008), and the possible preservation of fossil life in impact glasses on planetary surfaces  
539 (Schultz et al., 2014).

540

#### 541 **Acknowledgements.**

542 We thank N. Blanco and A. Tomlinson for sharing information about the location of the  
543 PG and discussions about their origin. We thank F. Gouttefangeas and L. Joanny for their  
544 help in SEM data acquisition and S. Perroud and K. Narea for their help in the field.  
545 Discussions with M. Jolivet about paralavas, with D. Marguerie and P. Pengrech about

546 melting conditions were very useful. This study was funded by the Programme National  
547 de Planétologie (INSU/CNES), Artemis projects (INSU-CNRS), OSU Rennes and Fondecyt  
548 project N° 3140562. C.L. also acknowledges ongoing support from the IEB (grant PFB-  
549 23) and Anillo SOC 1405. We thank Dr. Wolf Uwe Reimold and an anonymous reviewer  
550 for their help in the elaboration of the final manuscript.

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**Figure captions.**

798

799 **Fig. 1.** Satellite image (Google Earth) of the northern Atacama desert with locations of  
800 the Pica Glass fields: Puquío de Nuñez (PN), Quebrada de Chipana (QC), Quebrada de  
801 Guatacondo (QG) and NW of the town of Pica (NWP). Contour line spacing is 500 m. The  
802 Salars of Coipasa (SC) and Uyuni in the Bolivian Altiplano highlight the extent of the late  
803 Pleistocene paleolake Tauca.

804

805 **Fig. 2.** Field observations at Puquío de Nuñez. (a) Satellite image (Google Earth)  
806 showing locations where glasses were observed (yellow dots), <sup>14</sup>C ages and main  
807 paleomagnetic sampling (red stars). Elevation with contour line spacing of 10 m. The  
808 dashed thick black line indicates a tectonic flexure. (b, c) Field images showing outcrops  
809 with samples of dark glasses partially covering partially the ground. (d) Field  
810 photograph of a vitreous, dark green, vesiculated and irregularly shaped tabular PG on  
811 the surface. (e) Field photograph of a glass sample within the soil under a 5-10cm thick  
812 layer of sand.

813

814 **Fig. 3.** Field observations at Quebrada Chipana. (a) Distribution of silicate glasses and  
815 baked clays on a satellite image (Google Earth ) with elevation contour line spacing of 10  
816 m. Yellow dots indicate places where glasses and/or baked clays were observed. <sup>14</sup>C  
817 ages and paleomagnetic sampling (red stars) are shown on the map. Green polygon  
818 indicates the flat area with no trace of surface heating, located 50 m above the glass  
819 fields. (b, c) Field images of glasses in the westernmost area, (d, e) Silicate glasses  
820 overlying a 10 to 20 cm thick layer of red clays, (f) Field image of the layer of baked clays.  
821

822 **Fig. 4.** Plant imprints in glasses. (a) Photograph showing PG overlying a ~20 cm thick  
823 layer of silicified plants at Quebrada de Chipana; (b) Silicified wetland plant remains (cf.  
824 Cyperaceae); (c) Photograph of a sample of glass overlying a layer of plants (Quebrada  
825 de Chipana locality); (d) Silicified twigs within a vitreous matrix; (e) SEM observation of  
826 a twig showing the replacement of the plant by silica. (f) Upper surface of one PG sample  
827 showing grooves due to plant imprints (Puquio de Nuñez locality); (g) Plant imprint  
828 within a glass sample from the NW Pica area.

829  
830 **Fig. 5.** Microscope observations of glasses. (a) Transmitted light image of PG from PN  
831 with flow-like structure. (b) Reflected light image of iron sulphide (S) showing partial  
832 weathering-related oxidation (O). (c, d, e) Backscattered Electron (BSE) images of  
833 crystallite-rich glass with relict grains and dendritic overgrowths of feldspar and  
834 clinopyroxenes, typical of quench textures. (f) Iron sulphide grain nucleated on a vesicle.  
835 (g) Large sulphide grains in a vesicle. (h) Detrital grains in a glass matrix.

836  
837 **Fig. 6.** <sup>14</sup>C age determinations. Calibrated <sup>14</sup>C age spectra (thick lines for median ages,  
838 different colors illustrate different samples, see Table 1). (a) 6 samples from Puquio de

839 Nuñez. (b) 9 samples from Quebrada de Chipana. (c) 2 samples from NW of Pica and  
840 Quebrada de Guatacondo. The Mystery Interval (MI) and the Younger Dryas (YD) cold  
841 periods at the end of the Pleistocene are highlighted with the yellow boxes while the two  
842 phases of Central Andean Pluvial Event (CAPE) (Gayo et al., 2012) are shown in green  
843 boxes

844

845 **Fig. 7.** Magnetic properties and examples of paleointensity results. (a) Plot of the  
846 magnetic susceptibility versus the intensity of the NRM showing significant magnetic  
847 variations between the PGs at Puquio de Nuñez and Quebrada de Chipana or within the  
848 Quebrada de Guatacondo glass field; (b, c) Variation of the intensity of the NRM during  
849 alternating field demagnetization for silicate glasses and baked clays; Paleointensity  
850 diagrams and associated orthogonal plots for a sample of baked clay (d), silicate glasses  
851 at Quebrada de Chipana (e) and Puquio de Nuñez (f and g). Red filled symbols  
852 correspond to points used to determine the slope of the best-fit line in the NRM-TRM  
853 plot. Triangles correspond to PTRM checks. For orthogonal plots, open green (filled red)  
854 symbols are projection in the vertical and horizontal plane, respectively.

855

856 **Fig. 8.** (a) Equal-area projections of the paleomagnetic directions determined in  
857 oriented samples at Puquio de Nuñez (open, filled symbols for respectively negative,  
858 positive inclinations. (b) Paleomagnetic directions at Quebrada de Chipana (glasses  
859 shown in green circles; baked clays with red diamonds). (c, d) Paleomagnetic  
860 inclinations at Puquio de Nuñez and Quebrada de Chipana. (e) Geomagnetic  
861 paleointensities determined in samples from Puquio de Nuñez and Quebrada de Chipana.

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863

864 **Dataset captions**

865

866 **Dataset S1.** Chemical data of major, minor and trace elements in glasses and sands.

867 Whole-rock chemical data for the Pica Glass were obtained by ICP-MS.

868 Only major elements are reported for microprobe data of pure glasses.

869 XRF determination for whole rock data for sands. The accuracy is assessed by

870 comparison with reference samples.

871

872 Dataset S2. <sup>14</sup>C dating results obtained at “Plateforme Nationale LMC14”, Gif sur Yvette,

873 France

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876 **Dataset S3.** Paleointensity determinations in baked clays and glasses.

877

878 **Dataset S4.** Google Earth KML file with additional information

879