Pumice clasts in cross stratified basalt-dominated sandstones and conglomerates. Characteristics and depositional significance: Huarenchenque Fm (Neuquén, Argentina)

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ABSTRACT

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22 The Huarenchenque Fm is a Pleistocene clastic sedimentary unit that crops out 23 in the SW of the province of Neuguén, Argentina. This unit is made up of cross 24 stratified basalt-dominated sandstones and conglomerates with pumice clasts 25 accumulated in a fluvial context. The roundness of these pumice clasts, the 26 numerous fragments of volcanic glass (shards) and their association with 27 polymodal basalt-rich clasts in cross-bedded conglomerates strongly suggest 28 that these clasts were transported together during hydraulic flow. Pumice clasts 29 are usually buoyant in cold water whenever their density is lower than 1g/cm³. 30 However, since their density exceeds that of water during sediment transport, they form part of the sedimentary record. An artificial channel (ASSUT-1 flume, 31 32 University of Barcelona) was employed to yield fresh insight into the behavior of 33 these clasts mixed with sands during transport and accumulation processes. 34 The hydraulic equivalence of both materials was calculated by evaluating the 35 density of the pumice clasts and that of the quartz sands. The pumice clasts sank as a result of the interaction of pumice-rich pyroclastic flows with a moving 36 37 mass of shallow water. However, they retained their buoyancy after recovery

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from the sedimentary record (field outcrop). The sinking process is thereforerapid and reversible.

40 Key words: pumice clasts in polygenic conglomerate, sinking of pumice, pumice
41 water saturation, Neuquén Basin, Argentina.

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43 **1. Introduction**

44 The non-marine Huarenchengue Fm is characterized by cross-bedded and 45 clast-supported polygenic and polymodal unsorted conglomerates displaying 46 rounded, subrounded, subangular basalt, and rounded pumice clasts (Groeber, 47 1956; Holmberg, 1973; Zanettini et al., 2010). The conglomerates have an 48 unsorted sandy matrix with small lenses of clasts. Some levels of fine to very 49 coarse-grained conglomeratic sandstones are interfingered. Several pyroclastic 50 deposits are intercalated with conglomerate and sandstone levels locally (Stura 51 and Mazzoni, 1994). A number of lenticular to tabular levels of basalt-rich 52 sandstones (blue sands) display pumice-rich laminae (white-gray sands) made 53 up of pumice granules and shards. The Huarenchenque Fm that fills former 54 fluvial paleovalley varies considerably in thickness, attaining 80 – 100 m 55 towards Loncopué, whereas to the SE of the Neuquén province the values 56 attain 30 – 40 m. In conglomerates, a mixture of basalt and pumice clasts is 57 uncommon given their differences in density. Despite the occurrence of pumice 58 clasts in non-marine deposits in the fossil record, there are many data on their 59 sinking process in marine environments (Manville et al., 2002; Jutzeler et al., 60 2017). Several volcanic rock fragments are incorporated as clasts into different 61 fluvial contexts (Cole, 1991; Paredes et al., 2015; D' Elia et al., 2016) as a result 62 of reworking processes produced by hydraulic flows on previously accumulated

63 volcanic materials (Smith, 1987; Cole and Ridgway, 1993; Paredes et al., 2007; Sohn et al., 2013). However, these reworking processes rarely develop during 64 mixing of low and high-density clasts in a context of active fluvial systems. Such 65 is the case of the Huarenchengue Fm which displays large and small pumice 66 fragments acting as clasts ($D > 1 \text{ g/cm}^3$) coevally with pyroclastic deposits that 67 68 prevent them from being reworked. Our study seeks to gain a better 69 understanding of the sedimentological significance of pumice clasts that are 70 mixed with basalt clasts in a non-marine sedimentary record (Huarenchengue 71 Fm). We provide abundant evidence in support of the coeval transport of 72 pumice and basalt clasts in an active fluvial system.

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75 **2. Geological setting of the Huarenchenque Formation**

76 The studied area (Fig. 1) is located at Alto del Copahue-Pino Hachado in the 77 province of Neuquén near the Argentine-Chilean border. Geologically, it 78 straddles the boundary between the Loncopué Trough and the Northern 79 Precordillera of Neuguén (Ramos et al., 2011). The Loncopué Trough is a 80 Pliocene-Quaternary basin mainly filled with large effusive basalt-rich flows from 81 monogenetic volcanic vents. The morphology of basin floor is constituted by an 82 irregular topography developed on thick Mesozoic sedimentary deposits. The 83 Northern Precordillera of Neuquén, which was produced by a tectonic inversion 84 of Triassic - Jurassic halfgrabens, displays thick Jurassic and Cretaceous 85 deposits crossed by Cretaceous to Palaeogene volcanic and subvolcanic 86 intrusive bodies (D'Elia et al., 2016). The Huarenchenque Fm is situated in a 87 tectonic transitional area in the Neuquén basin. The northern sector underwent

88 a continuous compressive episode that gave rise to a mountain range, attaining 89 a height of 4000 m locally. The southern sector is characterized by alternating 90 compressive-extensive episodes that resulted in heights not exceeding 3000 m 91 (Folguera and García-Morabito, 2006). The area have a continuous volcanic 92 activity from the Miocene. The Huarenchengue Fm, which was formed along the 93 Pleistocene and Holocene, is the most recent volcano sedimentary 94 lithostratigraphic unit in Neuguén (Lambert, 1956; Leanza et al., 2001; Zanettini 95 et al., 2010). This unit crops out along the western and southern (austral) banks 96 of the Agrio River between latitude 38° and 38° 30' S and longitude 70° 20' and 70° 30' W and to the west of the Haichal and Liu Cullín creeks (Fig. 1). 97

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99 **3. Materials**

- 100 The Huarenchenque Fm, which is made up of basalt-dominated conglomerates
- 101 and sandstones containing pumice clasts, displays different facies
- 102 characterized by their composition and by their internal primary sedimentary
- 103 structures. The basalt-rich deposits form the irregular basement on which the
- 104 sandstones, conglomerates and pyroclastic rocks were laid down.

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106 3.1. Facies associations

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The clastic materials were studied applying the paleohydraulics for the analysisof cross laminations or cross stratifications. It should be pointed out that the

110 Pumice is made up of highly vesicular silicic to mafic glass foam that is usually 111 buoyant in water (Fisher and Schmincke, 1984). With a density lower than that 112 of water, Pumice is a product of silicic explosive eruptions (pyroclastic eruptions 113 or domes). Its behavior in volcanic and sedimentary processes is well 114 documented (Cas and Wright, 1987; Branney and Kokelaar 2002; Allen et al., 115 2008). To study the sedimentary characteristics of the Huarenchengue Fm, their lithofacies were classified in accordance with the system of Miall, (1977, 116 117 1978) and Rust (1978), which have subsequently been refined by other authors 118 for fluvial and alluvial-related deposits in volcanic settings (Smith, 1986, 1987; 119 Waresback and Turbeville, 1990; Zanchetta et al., 2004). In order to define 120 depositional settings, these facies were grouped into two different associations: 121 fluvial and pyroclastic.

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123 3.1.1. Fluvial facies association

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125 Two types of facies, volcaniclastic pebbly and sandy, are closely related in the 126 fluvial facies association. The conglomerates are moderately sorted and clast-127 supported. The clasts are subangular to rounded, and vary in size between 128 granule and cobble with a predominance of medium to coarse pebbles. Outsize 129 clasts (up to 50 cm) are common in some beds. The matrix is moderately sorted 130 volcaniclastic sand with grains varying in size from fine to coarse. Pebble 131 composition is dominated by basalt lithoclasts accompanied by (well rounded) 132 pumice fragments, and less commonly by muddy intraclasts derived from 133 reworking of the fluvial floodplain and/or bar tops. Conglomerate beds are 134 stacked or occur as single rock bodies and display both sheet and lenticular

135 geometries with basal sharp contacts. These deposits are characterized by 136 internal sedimentary structures such as planar and low angle stratification (Gh, 137 GI) and trough cross-bedding (Gt). The cross-bedded conglomerates occur as 138 laterally continuous deposits of three-dimensional gravel dunes (sets Gt) and as 139 infill of isolated scours or pools. These deposits show a basal, concave upward 140 surface and a progressive downturn in the dip of the foresets in a downstream 141 direction (Gp, Fig. 5). Internally, some conglomerate beds display normal 142 grading. Larger clasts (>10 cm) are usually imbricated with their longest axes 143 perpendicular to flow direction. However, in some instances, the scarcity of 144 elongated clasts prevents a reliable assessment of clast imbrication. Elongated 145 clasts are oriented subhorizontally in some places. Conglomerate beds consist 146 of moderately to poorly sorted, massive or crudely bedded, poorly imbricated, 147 clast-supported gravels with matrix rich in coarse sand and granules (Gm). 148 These beds are 0.3 to 0.5 m thick and vary considerably in terms of geometry, 149 ranging from laterally continuous beds to single scour fills. 150 The Huarenchengue Fm sandstones display a gradual variation in clast content 151 between sandstones and pebbly-rich sandstones. The lithofacies display 152 different modes of stratification (parallel laminations, low-angle and high-angle 153 cross-stratification). Bed thickness varies between 0.10 m and 1.50 m, on 154 average are around 0.30 m. In many instances, these beds are continuous 155 layers, scour and fill structures being rare. The sandy portion is made up of 156 volcaniclastics moderately sorted including subrounded to rounded basalt 157 and/or coarse pumice grains. The pebbles of the gravelly sandstones as well as 158 those of the thin gravel lineations are mainly rounded basalts. The composition 159 of sandstones is not uniform. Some beds (SI facies code) are made up of basalt

160 grains (blue sandstones) whereas others are rich in pumice clasts. An

161 alternation of basalt-rich and pumice-rich laminae in the foresets of cross-

162 bedded sandstones is also common.

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164 3.1. 2. Pyroclastic facies association

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166 Pyroclastic deposits are whitish to pale pink in color (Figs. 2, 3 and 4). They 167 consist of lapilli tuff beds in a vitric ash matrix. Lithofacies LT(1) is largely made 168 up of well sorted angular to subrounded pumice lapilli and coarse vitric ash. The 169 deposits are massive (sometimes with faint lamination), vary in thickness from 170 0.10 m to 0.40 m, and are usually intercalated in the volcaniclastic-rich fluvial 171 succession. Lithofacies LT(2) is composed of subangular to subrounded, matrix 172 to clast supported, pumice lapilli with scarce basalt blocks in a vitric ash matrix. 173 The main unwelded deposit of the volcanic facies is 400 m long and about 10 m 174 thick. Its basal section displays very poorly sorted dark gray massive 175 volcaniclastic pebbly sandstones with outsized and very angular basalt boulders 176 from the cliffs and screes bounding the paleovalley. The middle section consists 177 of light colored massive pumice lapilli with isolated angular volcanic blocks. 178 Towards the base are "pockets" and "lineations" of subrounded and rounded 179 basalt pebbles from previously deposited fluvial gravels. The lower surface of 180 this unit is sharp and irregular owing to scour and loading. The upper section 181 lies on a marked non-erosional surface. It is composed of pink pumice lapilli 182 with crude lamination and displays a reverse grading of pumice from middle to 183 top. Lithofacies LT(3) consists of a single 0.8 to 1 m thick lithosome 184 characterized by a bipartite alternation of light gray ash tuffs and lapilli tuffs that 185 are almost entirely made up of juvenile components. The deposits are parallel-

- 186 laminated and laterally continuous. Individual laminae are in the order of
- 187 millimeters to a few centimeters. This unit shows a faded cross-bedding towards
- 188 its basal part where its tangential geometry is displayed (Fig.6).

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190 3.2. Pumice in the sedimentary record

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192 Pumice, which has been studied for several decades, has a low density, which 193 contributes to its marked buoyancy in water (Fisher and Schmincke, 1984; 194 Witham and Sparks, 1986; Cas and Wright, 1987; White et al., 1997; Branney 195 and Kokelaar, 2002; Jokiel and Cox, 2003; Pattan et al., 2008). Large pumice 196 fragments have been known to drift over long distances across the oceans 197 (Richards, 1958; Coombs and Landis, 1966; Frick and Kent, 1984; Larsen et al., 198 2001; Risso et al., 2002; Bryan et al., 2004, 2012). However, small pumice 199 fragments that are waterlogged (Manville et al., 2002; Dufek et al., 2007; Vella 200 and Huppert, 2007; Allen et al., 2008; Patel et al., 2013) have a much higher 201 density. Consequently, the pumice sinks resulting in its addition to 202 sedimentation (Houghton and Wilson, 1989; Cashman and Fiske, 1991; 203 Manville et al., 1998; Riggs et al., 2001; Allen and Freundt, 2006; Fauria et al., 204 2017; Jutzeler et al., 2017). This accumulation is mainly produced by high-205 density currents (Sohn et al., 1999; Fülöp, 2001; Kataoka and Nakajo, 2002) or 206 by hydraulic currents (White et al., 2001; Manville et al., 2002; Fülöp, 2004; 207 Kataoka, 2005). Thus, pumice is incorporated into the sedimentary record as 208 bedload clasts in the main bedforms generated by hydraulic variations. 209

210 4. Experimental Methods

3.3.1. Volume of vesicles in Pumice

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213 The experiments were carried out with pumice from a quarry under exploitation. 214 Various samples from the Canary Islands (quarry of Cantos Blancos del Sur SL, 215 Tenerife) were examined to better understand the volume of vesicles and their 216 network in pumice. The dry and saturated weights of each sample were 217 evaluated on the assumption that the proportion of (cold or lukewarm) water 218 that could penetrate the dry pumice clasts during the experiments is not 219 significant. The volume of each pumice sample was then calculated. A 220 mechanical device was employed to sink the pumice in a beaker filled with 221 water. The errors in the detailed measurement of the free water surface level in 222 the beaker were attributed to the surface tension of the water, which produced a 223 meniscus. To minimize errors, a pipette was used to transfer water to the 224 beaker until the maximum level was reached and the first overflow was 225 produced. The volume of displaced water was controlled by means of high 226 precision scales. 227 For each sample, the volume and weight in dry conditions were determined and 228 compared with the weight of the sample whose vesicles were filled with water. 229 The volume of pulverized pumice (1 g) was calculated. Only when all these 230 values were obtained was it possible to determine the ratio of the vesicles and 231 their network of in the pumice, attaining values of about 80% and 90%, 232 respectively (Table I). These findings are consistent with the results of other 233 authors (e.g., Klug et al., 2002). 234

235 **3.3.2**. Hydraulic equivalences of pumice clasts and sediment grain-sizes

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237 A sound understanding of the hydraulic equivalences between the pumice 238 clasts and the sand is necessary to obtain the adequate pumice size to simulate 239 the sedimentary deposit in the laboratory. Using Stokes' law to describe the 240 depositional characteristics, it can be shown that the ratio of falling particle sizes 241 depends on the effective densities of the particles. The value of the guartz density used in the flume experiment was 2.65 g/cm³ and sand grains were 242 243 medium sized (0.25 to 0.5 mm). Water filled pumice samples of the 244 Huarenchengue Fm had densities ranging between 1.56 g/cm³ and 1.43 g/cm³. 245 The calculation of equivalent diameters of quartz and pumice using different 246 equations (Rubey ,1933; Tourtelot, 1968; Jutzeler et al., 2015) yields a pumice 247 diameter 6 to 10 times greater than those of guartz grains (about 3 to 5 mm). 248 After the pumice clasts (and/or shards) sink in an active fluvial environment they 249 are mixed with the clastic sediments carried by the turbulent currents and are 250 incorporated into the sedimentary record as part of the cross bedding or cross 251 lamination.

252 **3.4.** Experimentation

A series of experiments with a mixture of sands and pumice clasts was
undertaken in order to elucidate the behavior of pumice and other clasts of
different densities.

256 3.4.1. Sedimentary experiments

257 The experiments were carried out at the Assut-1 flume in the SIMGEO

laboratory of the Faculty of Earth Sciences at the University of Barcelona to

study a number of tractive primary sedimentary structures. These bedforms
were produced by the transport of a mixture of quartz sands and pumice clasts.
The pumice clasts sank rapidly in a beaker of water at room temperature
following exposure to steam.

263 **3.4.2.** Flume characteristics

264 The Assut 1 flume consists of a watertight channel of 15.20 m useful length, 37 265 cm in width and 40 cm in depth (Fig. 7). The lateral walls consist of reinforced 266 glass panels that allow the experiments to be visible without distortion. The 267 metallic floor is mechanized to eliminate any irregularities that could increase 268 the flume drag. The system is supported by a rigid structure that allows neither 269 flexures nor significant torsion. An elevation device enables the simulation of 270 variable gradients. The elevation is produced by hydraulic cylinders that act 271 upon the channel structure that pivots on a large hinge. The channel has two 272 sluices: one for the entry (apical area) and another for the evacuation (distal 273 area) of water flow. The effective depth of flow is controlled by the position of 274 the sluices that are driven by electrical mechanisms. Water, which circulates in 275 a closed circuit from the apical to the distal ends of the channel, proceeds from 276 a water storage tank equipped with a pump that drives the flow round the circuit 277 and then into a tank for sediment decantation, whence it is driven by means of 278 another pump to the initial water storage tanks.

279 3.4.3. Experimental procedures

The first experiment was carried out in a flume (Assut-1) placed in the building
of the Faculty of Earth Sciences of the Barcelona University (Fig. 9A) with

282 pumice samples from the Canary Islands and from Huarenchengue and la 283 Rinconada (locality close to Huarenchengue Fm outcrops). Pumice samples 284 from Iceland and Turkey were also used for comparison. A volume of about 10 285 liters (I) of pumice fragments with a grain-size between 3 and 5 mm was used. 286 A volume of about 60 l of quartz sand with a median grain size (0.5 - 0.25 mm)287 was also employed. In one experiment, the channel system was inclined, 288 attaining a height of 155 cm, equivalent to a general dip of 0.3° and maintained 289 in the same position throughout the process. The distal sluice had an angle of 290 60° that controlled a hydraulic jump generated at 6.5 m from the end of the 291 channel. The water supply was fixed at 10,000 liters/hour (l/h), which 292 corresponded to velocities of about 1.26 to 1.34 meters/second (m/s) at point 1 293 (Fig. 8). The linear water velocities are measured by means of MiniAir 20 294 current meter (provided by Schiltknecht, a Swiss Company) at the points 295 indicated in figure 8. After the hydraulic jump (a) between the points 1 and 2, 296 the velocity fell to about 0.38 to 0.42 m/s in points 3 and 4 respectively, whereas 297 downstream the velocities ranged from 0.31 to 0.09 m/s (6, 7 in Fig. 8), which 298 facilitated the generation of different types of tractive primary sedimentary 299 structures. Once the flume was stabilized, half of the sand (30 I) was added, 300 contributing to the generation of bedforms downstream of the hydraulic jump. 301 By contrast, at the other end of these sandy deposits, the velocities ranged from 302 0.09 to 0.15 m/s, resulting in the accumulation of very fine to fine-grained sands. 303 Thereafter, pumice samples were incorporated into the sediment and the 304 experiment continued until stabilization was achieved. Thus, the bedforms were 305 stabilized as a function of the grain-size of the clastic sediments and of the 306 water depth and flow velocity. Subsequently, the other half of the sand (30 I)

307 was added and the experiment continued for a further 30 minutes, resulting in 308 an accumulation of a pumice-dominated bed. This was then reworked and the 309 pumice clasts were carried away together with the sand, generating different 310 cross laminations with pumice clasts mixed with sandy sediments (B to F in Fig. 311 9). In another experiment, the position of the terminal sluice from 60° to 45° was 312 changed. Thereafter, the initial sedimentary accumulation underwent erosion 313 and all the sandy materials mixed with small pumice clasts were transported to 314 the end of the flume. The accumulated materials show sand-dominated and 315 pumice-dominated intercalations in tabular deposits. The pumice-rich layers are 316 not planar but have a gentle lenticular morphology (Fig. 9 B). The mixed 317 megaripples of medium sand and pumice are prominent (Figs. 9 C, D, E and F), 318 displaying characteristics similar to those studied at the outcrops of 319 Huarenchenque Fm.

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321 **4. Results of pumice clasts**

322 It is common knowledge that pumice is generated at high temperatures in 323 domes and in pyroclastic flows (Fisher and Schmincke, 1984; Jokiel and Cox, 324 2003). In our study, the theoretical high temperatures of the pumice-dominated 325 pyroclastic flow placements were simulated to determine their values. However, 326 the increase in temperature in the oven (600°C - 750°C) led to the melting of the 327 Huarenchenque Fm pumice samples, which resulted in the irreversible closure 328 of the vesicles. Heating pumice samples at variable temperatures (300°C – 329 600°C) produces their partial melting. Once the hot samples were placed in 330 water, a number of micro fractures appeared and water penetrated the pumice, 331 causing the samples to sink. Consequently, pumice buoyancy was lost.

332 By contrast, in the case of the Huarenchengue Fm samples, the buoyancy of 333 the interstratified pumice was not affected. This strongly suggests that the 334 temperature range of the pumice-rich pyroclastic flows were equal to or lower 335 than 300°C, when these reached the Agrio River. These values are consistent 336 with those obtained by other authors (Banks and Hoblitt, 1981; Cas and Wright, 337 1987). At the end of the experiments and after a short drying period, buoyancy 338 was restored in the pumice that did not undergo any significant change such as 339 cementation or fracturing. Pumice buoyancy was recovered when sampling in 340 the field outcrop. It strongly suggests that the pumice internal structure

- 341 remained intact when the pumice-rich flow reached fresh shallow waters.
- 342 4.1. Sinking processes of pumice

343 The presence of pumice clasts in a number of conglomeratic successions (Fig. 344 10 B, D) affords strong evidence that they sank and transported together with 345 clastic sediments. Thus, in a non-marine context as is the case of the 346 Huarenchengue Fm, the increase in density of pumice clasts probably occurs 347 during sediment transport by hydraulic flows. Our study of the internal structure 348 of pumice and their mixing with other clasts in the sedimentary record provides 349 fresh insights into pumice behavior. Despite the existence of isolated vesicles 350 that contribute to pumice buoyancy, electronic microscopy (DADES DEL 351 MICROSCOPI) reveals that the vesicles are interconnected by tiny ducts (Fig. 352 10 E, F) that facilitate sinking. Buoyancy is normally attributed to the high 353 vesicularity of pumice. If the vesicles are isolated (very low permeability) they 354 cannot retain enough water and the density remains below 1 g/cm³. By contrast, 355 and in several cases during pumice generation, some of the remnant gas may

be trapped in bubbles (Fauria et al., 2017) and buoyancy is maintained.

However if the vesicles are interconnected (high permeability) the air or gas can be displaced by water, resulting in density values >1 g/cm³. The surface tension of water also prevents air or gas from leaving the ducts. In our experiments, the best results of sinking processes were obtained from the interaction of steam with the pumice clasts when these were placed in water.

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5. Geochemical and mineralogical data

364 Pumice samples of different origin and composition were obtained for

365 comparison from the Canary Islands (Spain), Snaefellsnes and Askjia (Iceland),

366 Erciyes Dagi (Turkey) and from La Rinconada in the Neuquén basin (Argentina).

367 The chemical analyses of this pumice reveal a wide compositional range (Tabl.

368 II). The samples from the Canary Islands (La Granadilla area, Tenerife) are

369 phonolites whereas those from Iceland are mainly trachytes and dacites. The

370 pumice samples from Turkey are rhyolites and the ones from Huarenchenque

371 (FHCH) and La Rinconada are dacites with the exception of samples 8, 9 and

10 (FHCH), which are andesites. Despite their compositional diversity, no

373 significant differences were observed in their sinking processes.

The geochemical characteristics of all the samples were studied by means of

375 bulk-rock X-ray fluorescence for major elements. To this end, an energy

dispersive X-ray fluorescence spectrometer (S2 Ranger, Bruker/AXS GmbH,

377 Germany) equipped with a Pd target X-ray tube was used. The sample was

homogenized and crushed in an agate mortar until a grain size not exceeding

379 125 microns was attained. Material for analysis was prepared to obtain pressed

380 powder pellets in accordance with the procedures detailed in Marguí et al.,

381 (2009). Four scan runs for each sample were obtained at 10, 20, 40 and 50 kV. 382 The recorded EDXRF spectra were evaluated to determine their elemental 383 composition using the empirical calibration model consisting of twenty certified 384 reference materials. The results were processed by the software package 385 (DADES DEL SOFTWARE) linked to the instrumentation. Ten major elements 386 (Si, Ti, Al, Fe, Mn, Mg, Ca, Na, K and P), which were converted into oxides, 387 were analyzed. Total iron was expressed as Fe₂O₃. Analytical precision 388 exceeded ±2.5% (relative) for all major elements. The results were plotted in a 389 total alkali-silica diagram for chemical classification (Le Maitre et al., 2002) of 390 volcanic rocks (Fig. 11). According to these authors, each analysis was 391 recalculated to 100% on an H₂O and CO₂ free basis (Table II). Samples of 392 pumice from the Huarenchenque Fm are clearly plotted in the subalkaline field 393 and are mainly classified as dacites, and a few, as andesites. All of the pumice 394 samples show a significantly lower alkali content when compared with the main 395 evolutionary trend of the rocks from the Copahue-Caviahue volcanic complex 396 and other volcanic centers of the region (Kay et al., 2006) and most of them 397 have a high silica content (63-70%). By contrast, a basaltic pebble from the 398 same formation plots as a trachybasalt on the alkaline/subalkaline border. This 399 rock, although slightly differentiated, has a similar composition to that of the 400 olivine basalts of back-arc from the Loncopué trough (Varekamp et al., 2006) in 401 the Caviahue zone. The mineralogical study was carried out by means of X-ray 402 diffraction (XRD) analysis following the powder diffraction methodology for bulk 403 composition and oriented aggregates deposited onto a glass slide for 404 identification of clay minerals. XRD spectra were obtained in a Bruker 405 diffractometer (D2 Phaser model) equipped with a Cu target tube and a Linxeye

detector. The Huarenchenque samples are mainly amorphous, with low
crystallinity, showing small peaks that allow the identification of at least five
mineral phases (smectite, K-feldspar, amphibole, pyroxene and quartz). The
identification of the precise mineral species is currently not possible owing to
the low intensity of the identifiable peaks.

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412 **6. Discussion**

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414 The most striking finding of this work is that pumice clasts mixed with sands 415 give rise to diverse types of cross bedding and cross laminations. It is 416 noteworthy that basalt clasts and sands are mixed with some pumice clasts. 417 This seems a paradox given that large pumice clasts are usually buoyant in cold 418 water for long periods (Manville et al., 1998; Witham and Sparks, 1986) and 419 sink with difficulty. Several studies (Richards, 1958; Jokiel and Cox, 2003; Frick 420 and Kent, 1984; Mandeville et al., 1996; Pattan et al., 2008; Risso et al., 2002; 421 Coombs and Landis, 1966) have documented transport of floating pumices over 422 oceanic distances. Although pumice clasts are usually buoyant in cold water, 423 experiments carried out with boiling water and steam resulted in a rapid sinking 424 of pumice due to the displacement of internal air and other gases by steam with 425 the consequent absorption of water.

A simple experiment (Bargalló et al., 2013) demonstrates how the air in the
vesicles is displaced by steam whenever the pumice fragments are in contact
with boiling water. When the pumice is placed in cold or lukewarm water, the

429 temperature drops below the boiling point, resulting in rapid condensation. 430 Consequently, the resulting vacuum sucks the water into the vesicles, giving 431 rise to pumice saturation (waterlogging). All the pumice samples have an 432 interconnected vesicularity and their exposure to steam is the main reason for 433 their immediate sinking. One reason for the increase in density of these pumice 434 clasts could be that the steam penetrates their vesicles and cools. Large 435 amounts of steam were generated as the hot pyroclastic density current 436 reached the shallow waters of the Agrio fluvial system. In theory, some pumice 437 samples could be filled with different mineralogical assemblages, considerably 438 increasing their density, which would facilitate recycling and incorporation into 439 the transported sediments. This, however, is not the case of the pumice clasts 440 of the Huarenchengue Fm given the lack of evidence. 441 In the Neuquén Basin, the basalts of different origin (González and Vergara,

442 1962; Pesce, 1989) accumulated 45 My (Folguera and Ramos, 2000). It is 443 noteworthy that the largest volumes of basalts are not older than the Pliocene 444 (Ramos et al., 2011). The basalt clasts display different morphologies from 445 subangular to well and very well rounded, which suggests that their transport 446 was produced by rolling and impact processes. Some subrounded basalt clasts 447 such as second-generation clasts indicate that the previously accumulated 448 fluvial clastic materials were reworked. The well rounded pumice clasts also 449 suggest that they had undergone repetitive impacts (erosion) during transport. 450 Trituration generated numerous fragments (shards) of pumice (Pattan et al., 451 2008) that were incorporated into the unsorted sandy matrix. Thus, the pumice 452 clasts increased in density and were transported as bedload by large 453 discharges. It should be noted that locally the rounded pumice and basalt clasts

454 are of similar size because the fragile clasts (pumice) were easily eroded during 455 transport. Large number of fragments were incorporated into the cross bedding 456 of the blue sands as a result of the generation of different bedforms (hydraulic 457 dunes, megaripples). The vesicles of pumice have a network of tiny ducts that 458 allow the air-steam-water interchange. The experiments carried out in the flume 459 (Assut-1) provide ample evidence that the pumice and sands accumulated 460 together. If water had not penetrated the vesicles, buoyancy would have 461 remained intact and the pumice would not have been incorporated into the fossil 462 record generating primary sedimentary structures. The most reasonable 463 explanation for the immediate sinking of pumice clasts was the steam produced 464 by the hot pyroclastic flow as it came into contact with shallow fresh water. In 465 marine environments, submarine turbidity currents are generated when the 466 subaerial pyroclastic density current reaches water at the shoreline (Jutzeler el 467 al., 2017). In the conglomerate deposits, the mixing of pumice and basalt clasts 468 suggests that these clastic materials were transported together. In contrast, the 469 sandstone deposits display marked variations in grain-size. Thus, white 470 (pumice-rich) sandstones are coarser than blue (basalt-rich) sandstones 471 because of the hydraulic equivalence phenomenon. The cross bedded 472 sandstones and conglomeratic sandstones show foresets in the blue sands and 473 in the pumice-dominated materials owing to hydrodynamic variations during their transport. The coarse materials were poorly-sorted compared with the 474 475 sandy ones, suggesting that the rapid discharges and short flow duration 476 prevented sorting of the clasts despite their density contrast. The mixing of 477 similar-size high-density and low-density large clasts in the poorly sorted and 478 cross stratified conglomerates was brought about by the activity of supercritical

479 flows and not by high-density (hyper concentrated) flows. Thus, the behaviour 480 of these high-density flows do not allow the good development of cross-bedding. 481 The large cross bedding was due to the accretion in the frontal area of the 482 diagonal or transversal fluvial bars in a braided context and not generated by 483 migration of megaripples or hydraulic dunes. By contrast, the sandstones and 484 micro conglomeratic sandstones display textural variations because of the 485 differentiation of clasts produced during transport by subcritical hydraulic flows. 486 It should be noted that the marked large incision in the cross bedded 487 conglomerates is asymmetrical (Fig. 5). Initially, a major incision was generated 488 by a heavy discharge. Thereafter, a local cementation or hardening 489 (approximately 10 cm thick) of the scar surface probably occurred as a result of 490 the accumulation of volcanic ash. This contributed to the preservation of the 491 scar geometry after a subsequent discharge. The dip of prominent foresets to 492 the SE could have been produced by a subtle variation in flow direction or by a 493 marked increase in flow velocity. This event was probably without significance 494 and the scar geometry would have been maintained since the basal scar was 495 modified by a high velocity flow. But if the original geometry had been protected 496 by the hardening of the scar surface, the subsequent discharge would have led 497 to a downturn in the dip of the conglomeratic foresets to the SE. This was due 498 to a combination of high-energy events of gravel transport. The sedimentary 499 context was probably made up of longitudinal and transversal bars that were 500 generated in a gravel-dominated sedimentary environment (braided) that 501 underwent high discharges due to extensive snowmelt or ENSO "El Niño 502 Southern Oscillation" (Markgraf, 2001) episodes. Although it is not possible to 503 rule out some episodes of the ENSO such as the origin of large discharges

504 which could have affected the generation of the Huarenchengue Fm, no clear 505 evidence for this was found. Thus, these high magnitude discharges were 506 therefore caused by extensive meltwater as a result of the rapid Andean Last 507 Glacial Maximum deglaciation (Hulton et al., 2002; McCulloch et al., 2000). 508 Other possibility for the generation of sudden and large discharges could be 509 related to the eating of the volcanic edifice covered by thick snow 510 accumulations, when the magma reaches the surface resulting in a strong 511 snowmelt. The fluvial lithofacies described are typical of stream flow deposits 512 and are the result of rapid accumulation under fast-moving, sediment-laden 513 turbulent flows in gravelly braided streams with laterally unstable channels. 514 Ample evidence for this is provided by the scoured basal contacts, imbricated 515 clasts, clast-supported texture, and the absence of intervening fine-grained 516 deposits (Miall, 1977, 1978; Rust, 1978). Conglomerates, gravelly sandstones 517 and sandstones are interpreted as bedload deposits. Horizontally laminated and 518 low-angle inclined beds and reverse-oriented cross-stratified sets indicate high 519 energy supercritical flash flows. Trough and laterally continuous bedsets of 520 conglomerates were generated by frontal accretion of longitudinal bars, 521 whereas sandstone trough cross-bedded sets were deposited by waning flows 522 as a result of downstream migration of 3D dunes on bar tops and along their 523 margins or in secondary channels of the braided fluvial system. Cross-bedded 524 lenticular conglomerate lithosomes Gt(2) with a marked decrease in the dip of 525 foresets downstream (Fig. 5) are interpreted as the infill of isolated pools by 526 frontal and/or oblique bar progradation (Khadkikar, 1999). Moreover, the crudely 527 stratified conglomerates (Gm) were deposited by rapid suspension fallout with

some traction on the bed owing to turbulent hyperconcentrated flood flows(Smith, 1986; Sohn et al., 1999).

530 The LT(1) facies is a pyroclastic fall deposit accumulated rapidly. The facies 531 LT(2) rapidly accumulated due to pyroclastic density currents without tractional 532 grain segregation (Branney and Kokelaar, 2002). Variable grading patterns of 533 lapilli clasts strongly suggest a progressive aggradation because of turbulent 534 pyroclastic density currents in association with the waxing and waning of 535 volcanic eruptions (Sohn et al., 2013). The pyroclastic couplets of facies LT(3) 536 were produced by the passage of single density stratified surges such as those 537 recorded in modern eruptions (Fisher, 1990; Edmonds et al., 2005; Vazquez 538 and Ort, 2006). In such a context, the ash and lapilli tuff cross-stratified set 539 represents the downstream migration of surge-induced "progressive" sand 540 waves or dunes (Schmincke et al., 1973; Cole, 1991; Gençalioğlu-Kuşcu et al., 541 2007).

542 Chemical analyses of the clasts of pumice from the Huarenchengue Fm are not 543 consistent with the trend of the main volcanic rocks (Fig. 11) of the Copahue-544 Caviahue volcanic complex (Kay et al., 2006; Ramos and Kay, 2006; Varekamp 545 et al., 2006; Petrinovic et al., 2014). Thus, it is highly unlikely that these 546 materials originated in the Copahue volcanic area. The volcanic flows which 547 carried the pumice clasts to the former course of the Agrio river could not have 548 spread over so many kilometers from the volcanic vent. Consequently, the 549 primary origin of these volcanic materials must be traced to the areas 550 surrounding the outcrops of the Huarenchengue Fm. Thus, the volcanic vent 551 was probably located in the nearby uplift of Copahue-Pino Hachado. Rahue and 552 Butahuo volcanoes are only about 30 km to the west and the latest eruptions

have been dated at only 1 Ma (Tunstall and Folguera, 2005; Folguera andGarcía-Morabito, 2006).

555

556 7. Concluding remarks

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558 In theory, pumice clasts are buoyant if their vesicles are isolated. However, if 559 the vesicles are interconnected by tiny ducts, their buoyancy remains intact 560 since cold water does not penetrate the vesicles. But water is able to penetrate 561 pumice without difficulty under certain conditions. The sinking capacity of 562 pumice clasts was borne out by experiments in which pumice was exposed to a 563 column of steam. Samples from Iceland, Turkey and Argentina also underwent 564 experiments in a steam column. The behavior of these samples matched that of 565 the specimens from the Canary Islands. These samples sank rapidly when 566 placed in a beaker filled with water at room temperature. Although sinking 567 capacity does not depend on the chemical and mineralogical composition of the 568 pumice, it does depend on the number of vesicles and on their fabric 569 characterized by vesicle micro-connections. The vesicular interconnectivity may 570 attain high values. As the hot pyroclastic flow comes into contact with water a 571 large amount of steam is produced. The shallow water and the large surface 572 area, facilitated the generation of great amount of steam. The pumice clasts that 573 increase in density sink rapidly and are incorporated into the geological record. 574 This may account for the outcrops of the Huarenchengue Fm where the pumice 575 clasts are mixed with basalt clasts in the conglomerates and with basalt grains 576 in the sandstones. Since the area offers very little evidence of a main fluvial 577 valley or palaeovalley in the proximity of the present Agrio River, we may 578 assume that this river followed the same course from the Pliocene to the

579 Present. A large discharge is essential for the transport of the basalt-dominated 580 clastic sediments. The contact of the pyroclastic flow with the snowy areas at high altitudes near the Pino Hachado Caldera probably resulted in high 581 582 magnitude discharges. Such discharges attain velocities that carry vast 583 amounts of high-density clasts without sorting during transport. These 584 discharges are able to rework temporary dams in fluvial valleys that are 585 obstructed by pyroclastic or other deposits carrying many outsized clasts of 586 local origin. In the flume experiment, the behavior of the flow resulted in an 587 accumulation of cross bedded sediments (mixture of sand and pumice) has a 588 pattern similar to that of the facies displayed in the Huarenchengue Fm 589 outcrops. The sedimentary accumulation after the experiment shows a number 590 of small units limited by scars. The lower unit is characterized by large scale 591 and low angle cross bedding overlain by a central unit constituted by cross-592 laminated sands. The upper unit is made up of sandstones with plane beds. 593 The lower unit consists of sands deposited by critical flow (upper flow regime) 594 whereas the central unit corresponds to ripple progradation. The upper unit was 595 also deposited by critical flow (upper flow regime). The outcrop of the 596 Huarenchengue Fm exhibits a similar vertical trend. The lower unit (layer), 597 which displays large scale and low angle cross bedding, was brought about by 598 heavy discharges under critical conditions. The central unit resulted from the 599 accumulation of basalt-dominated sandy and clastic materials from hydraulic 600 dunes/bars, giving rise to transverse fill cross bedding under subcritical 601 conditions. The upper unit was produced by a large discharge that led to the 602 generation of plane beds and other associated bedforms. This suggests that the 603 sedimentary accumulation was episodic and that the variations in water velocity

604 were brought about by significant changes in discharge and in the snowmelt

605 due to subsequent eruptions of the Pino Hachado caldera.

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609

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893	FIGURE CAPTIONS
894	Fig. 1. Location of Huarenchenque in the Neuquén basin (upper left) in
895	Argentina (upper right). The box indicates the area under study. The main
896	outcrops are along the Agrio river banks.

897

898 Fig. 2. Outcrop at 38° 18' 22.5" S and 070° 36' 09.9" W, near Huarenchengue 899 where the basalt-rich scree deposits predate the first volcanic materials (facies 900 LT(1), LT(2)). The pumice clasts are the white ones. The position of samples 901 FHCH 0-8 is displayed. Overlying these materials are (shaded) fluvial deposits 902 (facies Gt). The basalt clasts (rounded) and fragments (angular) are the black 903 ones. The upper part is made up of basalt-rich scree accumulations. The legend 904 for the clasts and fragments is the same in all the figures. 905 906 Fig. 3. Outcrop at 38° 18' 52.4" S and 070° 35' 39.3" W near Huarenchenque. 907 The fluvial deposits are interfingered with volcanic materials. 908 909 Fig. 4. Outcrop at S 38° 19' 15.4" S and W 070° 35' 10.9" near Huarenchenque, 910 where the fluvial deposits predate the volcanic materials that are overlain by 911 other fluvial deposits. The intercalation of a massive conglomerate level (Gm) is 912 noteworthy. The position of the sample FHCH 10 is displayed. 913 Fig. 5. Outcrop of the Huarenchengue Fm at S 38° 31' 17.0" S and 070° 24' 914 28.7" W and the distribution of the main cross stratified deposits. Flow is from 915 right to left. The main facies are depicted by their specific codes. 916 917 Fig. 6. Detailed aspects of the outcrop displayed in Figure 5. (A) Lower unit of 918 SI. (B) Close up of the low angle and large scale cross bedding with imbricated 919 clasts. (C) Pumice-rich layer (small, rounded, light colored clasts) over cross-920 bedded blue sands. (D) Trough cross bedding caused by progradation of 921 hydraulic dunes. Close up of St (facies) in figure 5B. (E) The pumice-rich

922 lineation (light colored shards) denotes asymptotic cross bedding. (F) Blue

923 sands facies intercalated with prominent pumice-rich laminations.

924

925 Fig. 7. Conceptual arrangement of the Assut-1 flume. Floodgate dip variations 926 during the experiment. (A) The upper position of the terminal floodgate (angle 927 k) controls the position of the hydraulic jump (a) and the position (xa-xb) of the 928 deposit of sediments that display diverse bedforms (a-b). (B) The lower position 929 of the terminal floodgate (angle k') results in the reworking and progradation of 930 previously accumulated sediments. Note the shift of the sedimentary deposits 931 towards the flume exit and also the reduction of the distance from the position 932 (xa' and xb') of the deposits towards the end of the flume.

933

Fig. 8. Punctual variations of flow velocity that affect the sedimentary

935 accumulation in the Assut-1 flume during the initial experiment (Fig. 8). Average

velocities in meters per second (m/s) at the numbered points: (1).- 1.30 m/s;

937 (2).- 0.53 m/s; (3).- 0.42 m/s; (4).- 0.38 m/s; (5).- 0.43 m/s; (6).- 0.31 m/s; (7).-

938 0.09 m/s; (8).- 0.15 m/s.

939

Fig. 9. (A) Assut-1 flume in the SIMGEO laboratory; (B) Lenticular accumulation of pumice at the toe of the foresets of the main sedimentary form. Flow towards the observer. The flume is 37 cm in width; (C) Progradation of the bedform towards the right. The internal structure of the bedform is displayed by the interfingering of pumice-rich and sand-rich laminae. Scale in centimeters; (D) Cross-bedding generation as a result of the addition of sand when the bedform progrades to the left. Scale in centimeters; (E) New progradation to the left and

947 superimposition of the bedforms. Scale in centimeters; (F) Two superimposed 948 cross bedded deposits accumulate at the end of the experiment. The internal 949 structure of both deposits is magnified by alternation of sand-rich and pumice-950 rich foresets prograding to the left. The pumice clasts are therefore transported 951 together with the siliceous sands. Scale in centimeters.

952

953 Fig. 10. (A) Rounded composite cobble of the conglomerate deposits of the 954 Huarenchengue Fm. A mixture of pumice clasts (1) and basalt clasts (2) are 955 shown. (B) Well rounded basalt clasts (dark) displayed together with pumice 956 clasts (light). Pencil tip for scale. (C) Pumice clasts from the Snaefellsnes 957 volcano (Iceland) treated with steam are displayed at the bottom of a beaker 958 filled with lukewarm water. Coin (24 mm across) for scale. (D) Basalt-dominated 959 conglomerates with poor sorting. Note the subrounded basal clasts mixed with 960 rounded ones. Pencil is 15 cm in length. (E and F) Electron microscope images 961 of pumice clasts from the Canary Islands. (E) Original image. (F) Vesicle 962 interconnections (Red highlights). The small size of the vesicle interconnections 963 is noteworthy. The scale is the same in both images.

964

Fig. 11. Plot of the volcanic clasts included in the Huarenchenque and
Rinconada (FR) Formations on the TAS diagram (Le Maitre et al., 2002). Filled
circles: pumice; rhombus: basaltic clast. Crosses: pumice analyses from other
compositions used as comparison in this work. SN: Snaesfellnes, Iceland; ER:
Erciyes Dagi, Turkey; AS: Askjia, Iceland; AR: Arico, Canary Islands (Alonso et
al., 1988). Open symbols show the scattering of Plio-Quaternary volcanic rocks

971 from the Copahue-Caviahue volcanic complex (Varekamp et al., 2006).

972 Triangles: Copahue; squares: Caviahue.

973

974 **Table I.** Characteristics of some pumice samples from the Canary Islands used975 in the flume experiments.

976

977 **Table II.** Major-element compositions of volcanic rocks studied in this work.

978 Samples labeled FHCH- (except FHCH-9b) are pumice pebbles from the

979 Huarenchenque Formation. Sample FHCH-9b is a basalt pebble from the same

980 conglomerate as the pumice FHCH-9. FR is pumice from the Rinconada

981 Formation. SN, ER, AS, and AR are pumice from other localities and

982 compositions. SN: trachytic pumice from Snaesfellnes, Iceland; ER: rhyolitic

983 pumice from Erciyes Dagi, Turkey; AS: dacitic pumice from Askjia, Iceland; AR:

984 phonolitic pumice from Arico, Canary Islands (Alonso et al., 1988). Following Le

985 Maitre el al. (2002) each analysis was recalculated to 100% on an H₂O and CO₂

986 free basis.