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Paleoenvironmental Reconstruction Using Stable Isotopes And Trace Elements From Archaeological Freshwater Bivalve Shell Fragments In Northwest Patagonia, Argentina

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1	PALEOENVIRONMENTAL RECONSTRUCTION USING STABLE
2	ISOTOPES AND TRACE ELEMENTS FROM ARCHAEOLOGICAL
3	FRESHWATER BIVALVE SHELL FRAGMENTS IN NORTHWEST
4	PATAGONIA, ARGENTINA
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#### 31 ABSTRACT

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Stable oxygen and carbon isotopes (<sup>18</sup>O and <sup>13</sup>C) and the trace elements. 32 33 manganese (Mn) and strontium (Sr) were analyzed in archaeological bivalve 34 (Diplodon chilensis) shell fragments recovered from Parque Diana Cave, Patagonia, 35 Argentina, to analyze the temporal trends of human occupation of the North 36 Patagonia forest with climatic conditions recorded at regional scale but poorly known 37 at local scale for this site. We established a stratigraphic sequence of thirteen 10 cm 38 thick layers spanning the period c. 2370 BP to c. 580 BP and grouped these layers 39 into three cultural components 40 According to this region's climate, with rain and snow concentrated in winter and 41 dry summers, our data suggest that these components are contemporary with three climatic periods. A dry period indicated by high values of  $\delta^{18}$ Oshell,  $\delta^{13}$ Cshell and 42 43 Sr/Ca ratio (Mn/Ca ratio does not show any significant trend), in the Lower 44 component is associated with brief incursions of hunter-gatherers from the eastern steppe. In the Middle component, low  $\delta^{18}$ Oshell,  $\delta^{13}$ Cshell and Sr/Ca ratios, suggest 45 a humid climate with increased supply of meteoric and/or melt-water along with 46 47 terrestrial plants organic matter and soil carbonates to the river. According to the 48 archaeological evidence, in this period, hunter gatherers from the Pacific coast and 49 forest started to colonize the area across the Andes cordillera. At the beginning of the 50 Upper component, which is mostly contemporary with the expression of the Medieval Climatic Anomaly (MCA), the proxies are not totally coincident but a 51 52 tendency to progressively drier conditions could be inferred. Except for layer 4 for  $\delta^{18}$ Oshell and layer 5 for Sr/Ca ratio,  $\delta^{18}$ Oshell,  $\delta^{13}$ Cshell and Sr/Ca ratio show 53 consistently high levels in the Upper than in the Middle component. In layer 5, 54  $\delta^{18}$ Oshell and  $\delta^{13}$ Cshell are elevated with respect to the Middle component while 55 Sr/Ca ratio remains low. In layer 4,  $\delta^{13}$ Cshell and Sr/Ca ratio are high while 56  $\delta^{18}$ Oshell shows a negative peak. In layers 3 to 1,  $\delta^{18}$ Oshell,  $\delta^{13}$ Cshell and Sr/Ca ratio 57 remain at high levels, indicating an arid-warm climate with high aquatic plant 58 59 productivity, in coincidence with the expression of the MCA reported for this region 60 in a partially contemporaneous period (1080 - 1250 AD). At this time, the occupation 61 of the site by groups of the same origin as those present in the Middle component 62 became permanent. Extensive and intensive use of local resources in this period can 63 be inferred from the quality and quantity of artifacts recovered.

- 64 *Keywords*: Palaeoenvironment, Freshwater bivalves, Archaeology, Stable
- 65 isotopes, Trace elements, Patagonia.

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# **1 INTRODUCTION**

68	This paper reports a study of palaeoenvironmental changes recorded at the
69	archaeological site of Parque Diana Cave (PDC) Patagonia, Argentina. Our
70	methodology is based on the analysis of isotopic ratios ( $\delta^{13}C$ and $\delta^{18}O$ ) and trace
71	elements, manganese (Mn) and strontium (Sr) in shell fragments from the freshwater
72	mussel Diplodon chilensis (Gray 1928). The sequence of valves analyzed
73	corresponds to archaeological ecofacts accumulated through alimentary and
74	technological activities (Pérez and Batres 2008, 2010).
75	Two worldwide climatic events have been extensively described for a period
76	which is partially coincident with the period represented in the PDC sequence, the
77	"Warm Medieval Period" (sensu Lamb 1965), 800 - 1400 AD and the "Little Ice Age
78	(1400 -1700 AD, Soon and Baliunas 2003). Several authors have proposed that these
79	climate events have influenced cultural changes with material correlates in the
80	archaeological record (see Arnold 1992; Jones et al. 1999; Larson and Michaelsen
81	1990; Larson et al. 1994; Larson et al. 1996). The former event, which has also been
82	reported as "Medieval Climate Anomaly" (MCA) (Stine 1994), has been
83	characterized as a period of increased global average temperature with intermittent
84	and sometimes extreme droughts. The warm climate peaks of the MCA extended
85	over several decades, showing regional and even local (less than 100 km)
86	particularities (Bryson and Bryson 1997; Soon and Baliunas 2003). Thus, global
87	changes could have affected distant human populations synchronically but it is
88	necessary to know the magnitude of the changes occurred at local scale and the
89	historical context of each population in order to propose hypotheses related to
90	specific adaptive responses.
91	According to Dean et al. (1985), the impact of the climate on human societies
92	depends on four main factors: 1) magnitude, duration and frequency of the climatic
93	events; 2) Preexistent adaptive strategies; 3) the response of important natural
94	resources; 4) the size and density of the human group. Halstead and O'Shea (1989)
95	propose that human societies cope with the shortage of resources derived from
96	environmental changes by means of a wide range of practices which they defined as
97	"buffering mechanisms", These mechanisms can include, rules, myths alimentary
98	taboos, alternative agricultural practices, and food storage and exchange.

99 In archaeological research, climate events such as the MCA allow the observation of 100 the diverse adaptive responses of hunter-gatherer groups. For example, several works 101 suggest deteriorated climate conditions associated with relatively rapid and dramatic 102 cultural changes during the MCA in South West California (Larson et al. 1994; 103 Larson et al. 1996; Raab and Larson 1997; Jones et al. 1999). The latter authors 104 reviewed the main cultural responses for South West USA during MCA, which can 105 be summarized as four basic strategies: 1- social complexity; 2- mobility, 106 abandoning areas which had limited resources, e.g. those in the Mojave desert and, in 107 colonial times, deserting of the Santa Bárbara channel by the Chumash population 108 towards the Jesuit missions at the California channel 3- Resource intensification: a 109 wide range of passive or active practices aimed to widen the subsistence system by 110 exploiting a wider diversity of plants and animals and/or larger and more varied 111 foraging areas (Halstead and O'Shea 1989). The mechanisms recorded for the MCA 112 include increased dependence on storage (Testart 1982), production of goods for 113 exchanging at long distances (Arnold 1992), technological innovations (Jones et al. 114 1999), and economic diversification (Halstead and O'Shea 1989). For example, 115 Larson et al. (1994) proposed that long drought periods produced a stress condition 116 related to food shortage, stimulating the population of the Santa Elena channel to 117 intensify their diet by consuming an increasing variety of marine resources; while 118 other authors like Arnold (1992) suggested the production of necklace beads made of 119 mollusk shells by island groups for trading with inland groups; 4- Territorial 120 behavior: apparently, another consequence of MCA was the competition for scarce 121 resources, both from marine and terrestrial sources (Jones et al. 1999). The 122 necessities to control food resources and to remain next to reliable freshwater sources 123 seem to have further consolidated the populations territorial limits and fostered their 124 territoriality. For example, in sites at the central coast of California, the diets were 125 not widened and the commerce horizons were retracted, producing demographic 126 problems, which were not solved by adaptive adjustments or population mobility 127 (see Larson et al. 1994).

128

# 129 **1.1 Patagonia**

The climate of Austral Patagonia (Fig. 1) during the Holocene has been subject of
many palaeoclimatic reconstructions. Favier Dubois (2004) reviewed the previous

132 palaeoclimatic data, proposing a correspondence between the beginnings of the

development of the palaeosol named "Pedologic Event Magallania" and the expression 133 134 in Austral Patagonia of climate anomalies related to the MCA. This event has been 135 reported to occur contemporarily in North America and in Austral Patagonia (Jones et 136 al. 1999; Larson and Michaelsen 1990; Larson et al. 1996; Stine and Stine 1990; Stine 137 1994). Stine 1994 compared data from this period between California and Austral 138 Patagonia, reporting marked changes in humidity. From these data he suggested that 139 this was a global event and that, in the Americas, the changes in the precipitation regime 140 were probably more important than those in temperature. In the last decades, the 141 number and the resolution level of palaeoclimatic studies have greatly increased (Kilian 142 and Lamy 2012). Recently, Echeverría et al. (2017) have reconstructed the palaeohydric 143 balance variations of forest, steppe and ecotonal areas of Austral Patagonia during the 144 Holocene by analyzing pollen data obtained from seven sites and discussing previous 145 literature (Fig. 1). These authors have proposed a general trend for the eastern side of 146 the Andes range, with the intensity of the southern westerly winds (SWW) and 147 precipitations being positively correlated in the western forest areas, less positively 148 correlated in the forest-steppe ecotone and negatively correlated in the steppe. This is 149 coincident with data from numerous studies reviewed by Kilian and Lamy (2012), 150 which show a high positive correlation of SWW intensity and precipitation in the west 151 side of the Patagonian Andes, this correlation decreases towards the east, reaching 152 slightly negative values in extra Andean Patagonia. The resulting West-East humidity 153 gradient has varied in intensity along the Holocene due to asynchronic changes in the 154 precipitation regimes of forest, forest-steppe and steppe environments (Echeverria et al. 155 2017).

156 In contrast with Austral Patagonia, there are few palaeoclimatic reconstructions 157 covering the late Holocene in North Patagonia. Villalba (1990, 1994) has studied 158 growth rings from 1120 alerce (Fitzroya Cupressoides (Molina) Johnston 1924) trees in 159 the area of Río Alerce (Río Negro province, about 400 km southwards of the PDC, Fig. 160 1) and established the following chronology: Cold-wet, 900 - 1070 AD / Warm-dry, 161 1080 - 1250 AD, corresponding to MCA / Cold-wet, 1280 - 1670 AD with peaks in 162 1340 and 1650, related to the European Little Ice Age. This chronology is coincident 163 with results reported for Austral Patagonia (e.g. Moy et al. 2008) but differs from others 164 (e.g. Fey et al. 2009). Discrepancies between studies performed in North and South 165 Patagonia could respond to climatic factors such as those explained by the atmospheric 166 circulation model described for this period by Labraga (1997) (Favier Dubois 2004).

Alternatively, regional scale differences could be related to the ecologic factors
described above, e.g. differential effects of SWW on forest and steppe environments
(Echeverría et al. 2017; Fey et al. 2009; Garreaud et al. 2013; Kilian and Lamy 2012).

### 171 **1.2** Diplodon chilensis

172 The long-lived freshwater mussel Diplodon chilensis (Hyriidae) is common and 173 abundant in rivers and lakes of Northwest (Andean) Patagonia, Argentina (32°52' S; 174 68°51' W to 45°51' S; 67°28' W, Bonetto 1973) and in Southern Chile (34° 58' S; 175 71° 48' W to 46°37' S; 74°10' W, Parada and Peredo 2002). D. chilensis constitutes 176 an abundant and predictable freshwater resource throughout the year and is the most 177 frequently found mollusk in archaeological deposits from continental Patagonia 178 (Pérez and Batres 2010). Valves of this species have been frequently found in 179 archaeological sites in the western side of The Andes, from the transition between 180 the early and middle Holocene. This includes Andean sites, such as Alero Marifilo 1 181 (Mera and García 2004), Pucón VI and Colicó 1 (Navarro et al 2011) and Central 182 Valley sites, Alero Quillén 1 and Alero Quilo (Jackson and Jackson 2008). However, 183 these valves have not been used for paleoenvironmental reconstruction so far.

184

# 185 **1.3 Parque Diana Cave (PDC)**

186 The PDC is a rocky shelter which allowed us to establish the temporal sequence 187 of human occupation of the "Meliquina Archaeological Locality" (MAL). This 188 locality includes five archaeological sites with a potential functional linkage, and is 189 located 18.5 km South West of San Martin de los Andes city, within the Lanín 190 National Park, (40° 19´ S 71° 19´ W), at an altitude of 970 masl (Fig. 1). This area is 191 part of the "Andino-Patagónico Forest" phytogeographic region, which extends on 192 the hillside of both slopes of the Andes mountain range. On the Argentine side, this 193 region limits to the East with the Patagonian steppe, a vast semi desert-desert area, 194 which stretches eastwards to the Atlantic coast. The climate in MAL is moderately 195 cold and wet, typical of North Patagonian Andes. Rain and snowfalls occur mostly in 196 winter with 1500 to 2000 mm annual average precipitation. Figure 2 shows details of 197 the excavation and part of the PDC walls.

198 The sedimentary layer of PDC is presently 2 m deep (Fig. 3). Due to the site's 199 location, the main agents of accumulation are the natural disaggregation of mother 200 rock and, to a lesser extent, external sources, through deposition of small wind-borne

particles. Another accumulation factor is the recurrent use of the shelter by human
groups and animals (Pérez et al. 2008). Our analyses derive from three assemblages
of faunal remains, defined as Lower, Middle and Upper cultural components. The
nearest provisioning source of *D. chilensis* to the PDC is a shallow bank of the Río
Hermoso, 50 m from the site.

206 The Lower component (present only in PDC) comprises layers 9 to 12, 1.2 to 1.5 m 207 from current ground level. Layer 9 and most part of layer 10 contain large blocks of 208 mother rock, which separate them from the lower layers. The Lower component has 209 been radiocarbon dated at layer 10 to  $2370 \pm 70$  BP (233-762 cal. BC, LP-1704 vegetal coal, 2 sigma <sup>14</sup>C age calibration using Calib 3.0 software, Stuiver and Reimer 1993) 210 211 and shows a low frequency of human activity. This occupation corresponds to a 212 transient camp in a late exploratory stage of the area (Borrero 1994-1995), by hunter-213 gatherers (Pérez 2010). The diet faunal components (no cervids and few D. chilensis 214 remains), the kind of lithic and animal raw materials (e.g. petrified wood, which is 215 available in specific zones of the steppe but not in this area and guanaco bone) and the 216 technology used suggest groups coming from contemporary steppe occupations, such as 217 Casa de Piedra de Ortega and Epullán Grande cave, in the upper Limay River basin 218 (Crivelli Montero 2010, Fig.1). The lack of evidence on the use of local alimentary 219 resources or raw lithic materials along with the absence of debitage from tool 220 manufacturing, suggest that these groups were just exploring the zone (Pérez 2010). 221 Between the Lower and Middle components, there is a discontinuity of about 222 1000 years in the artifactual or ecofactual remains, associated to detachment of 223 mother rock from the walls. This event made PDC unsuitable for human occupation 224 until wind-borne sediments and animal remains (rodent bones and excrements) made 225 the surface regular again.

226 The Middle component, dated at layer 8 to  $990 \pm 60$  BP (901-1206 cal. AD, LP 227 1720 vegetal coal) and layer 6 to  $900 \pm 60$  BP (1018-1264 cal. AD, LP 1713 vegetal 228 coal), shows the first evidence of contemporary open sites, which might have been 229 functionally linked to PDC (Pérez 2010). These sites are in the form of localized 230 accumulations or concentrations of vegetal coal, separated one from each other by up 231 to 300 m along the banks of local streams and Lake Meliquina and suggest sporadic 232 occupation of the area with low reoccupation rate. The lack of steppe resources and 233 the predominance of forest and lacustrine resources among the remains, suggest that 234 these hunter-gatherer groups had a better knowledge of the environment. These

archaeological features can be attributed to a period of colonization (Borrero 1994-235 236 1995) by people who already possessed technological advantages to effectively exploit forest environments from Central-South Chile (Pérez 2010). These people 237 238 were complex societies characterized by a hunting, gathering and fishing economy 239 with, at least, access to cultivated plants or products derived from corn. They 240 possessed pottery technologies (including patterned decoration, incised and painted 241 by reserve technique), and used native metals such as copper, among other features 242 (see Hayden 1981, 1995). In this component, the archaeological evidence shows a 243 gradual replacement of artifacts manufactured with non-local raw materials by others 244 manufactured with local rocks, e.g. obsidian characterized by the chemical groups 245 found in the nearby area (Pérez et al. 2019) and use of local clay for pottery (Pérez 246 2010). This suggests a gradual increase in knowledge, interaction with and use of 247 local resources. The faunal remains associated to these sites are predominantly, if not 248 exclusively, from forest and freshwater environments, and include necklace beads 249 and artifacts made from Pacific mollusks shells, which are progressively replaced by 250 shells from local freshwater mollusks (Pérez and Batres 2010). The vegetal remains 251 include the first record for Argentinian Patagonia of Gevuina avellana nuts (Pérez 252 and Aguirre 2019) plus the most austral evidence of cultigens such as maize for pre-253 Hispanic America. Both vegetal resources have also been recorded in 254 contemporaneous archaeological sites in forest areas of the Chilean Andes and 255 Central valleys (Adán and Mera 2011; Adán et al. 2016; Pérez and Erra 2011; Pérez 256 and Aguirre 2019). 257 The Upper component is dated in layer 3 to  $760 \pm 60$  BP (1163-1388 cal. AD, LP 258 1697 vegetal coal) and layer 2 to  $580 \pm 60$  BP (1289-1439 cal. AD, LP1695 vegetal 259 coal). This component includes 300 years of artifacts and ecofacts deposition, between

260 0.3 and 0.8 m deep from the current ground level. This component shows the site's 261 highest richness and variability in archaeological remains. It is characterized by the 262 superimposition of structures related to combustion and/or the maintenance of artifacts. 263 This is the period of most stable and recurrent occupation of MAL, with enhancement 264 of the tendencies observed in the middle component, both in PDC and in the open sites 265 placed on the coast of Lake Meliquina. The number of elements characteristic of the 266 contemporary populations of the Western side of the Andes is increased, including the 267 presence of copper artifacts. The interaction with the environment is more evident in 268 this component, with local production of pottery elements with adequate size and shape

to efficiently collect and process a great variety of vegetal and animal food items from 269 270 freshwater and forest sources (Pérez 2011), including the preparation of fermented 271 beverages (Pérez et al. 2016). This tendency is also evident in the selective use and 272 management of the sources of lithic raw materials such as obsidian (Pérez et al. 2019), 273 resulting in changes in the shape of extractive elements such as arrow points, among 274 other evidences of technological specialization. The absence of steppe materials, along 275 with the use of the forest resources, accompanied by a minor portion of Pacific coast 276 species, shows the reoccupation of the area by the same groups that had been in this 277 region since about 900 AD (Pérez 2010; Pérez and Batres 2010).

The aim of this work is to reconstruct a palaeoclimatic multiproxy sequence with adequate scale and resolution to discuss the climatic-environmental events associated to the human occupations of MAL. We hypothesize that certain parts of the North Patagonian forest-lake area were appraised during warm and/or dry episodes framed in a climatic anomaly period registered at a bigger scale but whose expression at local scale is still unknown.

The predictions for contrasting this hypothesis are: a) There is a correlation between environmental changes and human behavior in the MAL cultural sequence; b) These changes must give some advantages for human occupation to the forest environments on the East of the Andes; c) Some variables inherent to these changes, such as intensity and duration should influence cultural responses, such as mobility, technological change, economic intensification and territoriality.

### 290

291

# 2. MATERIALS AND METHODS

292

# 293 2.1 Sediment analysis

In order to detect possible differences among layers in the quality and quantity of the bivalve remains recovered due to taphonomic problems related to soil quality, sediment pH and the shell fragmentation index (Grayson 1984), adapted to bivalves by Batres (2008), were measured throughout the stratigraphic sequence.

298

#### 299 2.2 Shell analysis

300 This study is based on 168 specimens, identified as *D. chilensis* whole shells and

- 301 shell fragments, according to the number of identified specimens (NISP) defined by
- 302 Grayson (1984), recovered from the PDC (Fig. 4). Samples were obtained from

10cm thick layers, which were subsequently combined into three units or 303 304 components to correlate the obtained results with relevant aspects of human behavior 305 in the frame of an ecological model of space utilization in Patagonia (Borrero 1994-306 1995). For stable isotopes, we analyzed one fragment per layer (10 layers containing 307 valve fragments) plus two additional samples for each of the radiocarbon dated 308 layers excepting layer 8, from which only one additional sample could be obtained. 309 One fragment per layer was split in two halves. One half was used for measuring 310 stable isotopes and the other was analyzed for Ca and trace elements (see below). We 311 analyzed valve fragments larger than 5x5 mm; representing valve growth of 2-8 312 years.

313 Stable isotopes were analyzed with a Delta S Finnigan Mat triple collector

314 spectrometer, at the INGEIS, Buenos Aires by the method developed by McCrea

315 (1950) with minor modifications. Carbonate was converted to  $CO_2$  with  $H_3PO_4$  at

 $316 \quad 60^{\circ}$ C. CO<sub>2</sub> was purified in a vacuum line, using cryogenic traps to eliminate other

317 volatile compounds and analyzed by mass spectrometry.  $\delta^{13}$ C and  $\delta^{18}$ O values were

318 reported relative to standard V-PDB (Vienna-PeeDeeBelemnitella) (Coplen 1994),

319 with errors of  $\pm 0.1$  and  $\pm 0.05$  ‰, respectively.

320 The trace elements Mn and Sr, and Ca were measured on 10 shell fragments, one half 321 of fragment per layer. Shell fragments were washed with 5mM EDTA solution to 322 remove externally adhered ions and then digested in a microwave oven with nitric acid 323 and hydrogen peroxide (2:1, v/v). Organic matter was separated as an insoluble film, 324 which accounted for ca. 5% of the sample mass. Gallium was added to these 325 dissolutions, as internal standard. Aliquots of 10 µL were placed in a quartz reflector for 326 analysis by total X-ray reflection fluorescence (TXRF) (Prange and Schwenke 1992). 327 Spectrum evaluation and quantitative analysis were performed using the QXAS 328 software package from IAEA, using least-square regression analysis and calibration 329 curves within the range 1–20 ppm. Detection limits were 0.02 and 0.05  $\mu$ g/g, for Mn 330 and Sr, respectively, with an error of 10% (See Sabatini et al. 2009 for more detailed 331 explanation of the method). Results were expressed as element/Ca ratio x 1000. 332 To compare trace element proportions, Mn, Sr, Fe and Zn were measured as 333 described above for Mn and Sr in duplicate on valves of D. chilensis taken alive from 334 Río Hermoso near the PDC and in water samples from the same site. The relevant 335 literature to support and interpret paleoenvironmental reconstruction based on the

- analysis of stable isotopes and trace elements in mollusks shell remains is described
- in Appendix A.
- 338

# 339 2.3 Interpretation of the palaeoenvironmental data

340 Soldati et al. (2009; 2010) have characterized summer and winter growth bands in 341 valves of living individuals of D. chilensis from about 150 km south to our study site. These authors report low  $\delta^{18}$ O in summer bands, assigning these values to higher 342 343 temperatures according to previously published data (Dunca and Mutvei 2001; Dunca et 344 al. 2005; Schöne et al. 2004). High Mn/Ca, Sr/Ca and Ba/Ca ratios have also been detected in these summer bands (Soldati et al. 2009). Low  $\delta^{18}O_{shell}$  in summer growth 345 346 lines could be related to the effect of temperature on isotopic fractionation during shell 347 carbonate deposition (Carré et al. 2005; Dettman et al. 1999; Epstein et al. 1953; 348 Gordillo et al. 2015; Grossman and Ku 1986; Yoshimura et al. 2010). However, Soldati et al. (2009) have reported that the temperature cycles calculated from  $\delta^{18}O_{shell}$  and  $\delta$ 349 350 <sup>18</sup>O<sub>water</sub> underestimate the actual summer-winter difference in their study site. Among other hypotheses, these authors have suggested that such underestimation could respond 351 to seasonal changes in  $\delta^{18}O_{water}$  which, in turn, affect *D. chilensis*  $\delta^{18}O_{shell}$ . 352 In the area of the present study, precipitation is concentrated in winter and stream 353 354 discharge is high in winter-spring. During relatively humid years, high altitude wetlands 355 and lakes accumulate water, and snow remains in the mountains until summer. Therefore, during such years, rivers like the Río Hermoso receive abundant <sup>18</sup>O-356 depleted water from lakes and streams fed by melt-water throughout the year. Under 357 such conditions, the effect of evaporation would be small and low  $\delta^{18}O_{water}$  and  $\delta^{18}O_{shell}$ 358 would be recorded in summer. In contrast, during arid periods, snow is already absent in 359 spring and high-altitude reservoirs with meteoric water are reduced or even depleted in 360 summer. This reduced input of <sup>18</sup>O-depleted water along with higher evaporation would 361 increase  $\delta^{18}O_w$  in Río Hermoso with respect to humid years. Accordingly, reduced 362 stream discharge and increased evaporation to precipitation ratio have been previously 363 reported to reduce or even overcome the effects of temperature on  $\delta^{18}O_{shell}$  (Bar-Yosef 364 Mayer et al. 2012; Gajurel et al. 2006; Kaandorp et al. 2003; Marwick and Gagan 2011; 365 366 Schöll-Barna 2011; Versteegh et al. 2010; 2011). As we have analyzed the total 367 carbonate content of shell fragments, which span several years of shell growth, our data 368 reflect the combined effects of the hydrological and environmental parameters described 369 above, averaged among seasons.

- Kaandorp et al. (2003) have reported covariance of  $\delta^{13}C_{water}$  and  $\delta^{18}O_{water}$  from an 370 371 Amazonian floodplain with high records of both heavy isotopes during dry periods and with  $\delta^{13}C_{\text{shell}}$  and  $\delta^{18}O_{\text{shell}}$  responding to water composition. These authors relate 372 the increased  $\delta^{18}O_{water}$  to a strong evaporation effect, while elevation of  $\delta^{13}C_{water}$ 373 374 could be responding to depletion of the light isotope due to selective uptake by 375 aquatic plants. On the other hand, Gajurel et al. (2006) have reported that  $\delta^{13}C$  of 376 dissolved inorganic carbon in Himalayan rivers decreases downstream because of 377 soil derived alkalinity and land plant productivity. Additionally, increased 378 phytoplankton productivity or terrestrial plant material input to the river can 379 stimulate mussel metabolic activity, which in term would lead to higher proportion of 380 metabolic C being deposited in the shell and thus to lower  $\delta^{13}C_{\text{shell}}$  (see McConnaughey and Gillikin 2008, for a review). 381 382 High Mn/Ca ratio has been reported as an indication of high aquatic primary 383 productivity (Langlet et al. 2007; Carroll and Romanek 2008). Particularly for D. 384 chilensis, which shows maximum growth rate in winter (Soldati et al. 2009; 385 Rocchetta et al. 2014), Risk et al. (2010) have detected Mn peaks in winter growth 386 lines interpreting that increased precipitations and river discharge can augment 387 erosion, liberating soluble Mn. According to Lee and Wilson (1969), Sr/Ca ratio is 388 expected to show positive correlation with reduced river discharge and/or with 389 increased evaporation. However, trace element ratios are not easy to interpret and 390 should, thus, be interpreted in combination with other proxies (Peacock and Seltzer 2008). In this regard, Sr concentration has been reported as covarying with  $\delta^{18}$ O in 391 392 fossil shells of *Diplodon longulus*, high values of both variables indicating dry 393 season (Kaandorp et al. 2006).
- 394

### **395 2.4 Statistics**

396 Consistency among the different proxies was analyzed by Spearman correlation. 397  $\delta^{18}O_{shell}$  and  $\delta^{13}C_{shell}$  values were compared between the upper and middle 398 components through Student's t test. Results were considered significant at P < 0.05. 399

400 3 RESULTS AND DISCUSSION

# 401 **3.1 Sediment analyses**

Sediment pH ranged from 7.3 to 7.9 (Table 1). This slightly alkaline soil favored
the preservation of archaeological materials, especially CaCO<sub>3</sub> containing shells, as

was previously reported for similar environments in North Patagonia (see Pérez et al. 404 405 2008 and citations therein). The fragmentation index (Grayson 1984, modified by 406 Batres 2008) showed that, various taphonomic processes acted in the Lower 407 component. The high rates of sample fragmentation found in layers 9 and 10 408 coincide with the lowest NISP for the site. In the Middle and Upper components, pH 409 was almost constant. NISP values, in the Middle component are higher than in the 410 Lower one. A trend to increased bivalve collection by human groups is evident, 411 although NISP remains low. The Upper component shows the largest number of D. 412 chilensis shell remains. The fragmentation index remains constant between the 413 Middle and Upper components, which indicates that the larger number of items 414 recovered in the Upper component is not due to lower taphonomic factors but to 415 increased bivalve collection activity (Table 1). 416 417 3.2 Trace elements in modern shells and water samples 418 Mn, Sr and Fe were present in shells and in water at similar proportions. Table 2 419 shows Ca and trace element concentrations in Río Hermoso water and in valves

420 taken from live mussels collected from the same site.

421

# 422 **3.3 Stratigraphic analyses**

423 Due to sample limitation, trace elements were measured in one valve fragment per 424 layer while stable isotopes were measured in three fragments from layers 2, 3, 6, and 425 10, two fragments from layer 8 and one fragment from layers 1, 4, 5, 7, and 9. 426 Therefore, we interpreted our results taking into account that results from only one 427 fragment should be analyzed with care. Spearman analysis showed significant correlation between  $\delta^{18}O_{\text{shell}}$  and  $\delta^{13}C_{\text{shell}}$  only after excluding data from layer 9, 428 which showed an extremely high  $\delta^{18}O_{shell}$  value (P = 0.037, R = 0.71). Similarly, 429  $\delta^{18}O_{\text{shell}}$  shows good correlation with Sr/Ca ratio if layer 9 is excluded (P = 0.024, R= 430 0.75).  $\delta^{13}C_{\text{shell}}$  and Sr/Ca ratio are also correlated (P = 0.0154, R = 0.83) only if data 431 from layers 5 and 7 are excluded. These correlations are consistent with the results 432 reported by Risk et al. (2010), who have found similar peaks of  $\delta^{18}$ O and Sr/Ca and 433 434 Ba/Ca ratios in the same species in Chile in summer growth lines, considering that 435 summer is the dry season in both Chilean an Argentine Patagonia. In our study, the 436 Mn/Ca ratio was not considered for the analysis because it does not show any significant trend along the sequence and is not correlated with the other proxies. All 437

438 the data excluded from the correlation analyses correspond to layers in which only439 one shell fragment was used.

The Lower component shows high  $\delta^{18}O_{shell}$  and  $\delta^{13}C_{shell}$  along with high Sr/Ca 440 441 ratio in layer 10 (Fig. 5), suggesting arid conditions according to Kaandorp et al. 442 (2006). Similarly, Echeverría et al. (2017) have reported negative palaeohydric 443 balance for several forest environments of Southern Patagonia during a period which includes the corresponding to this component. The  $\delta^{18}O_{shell}$  value recorded in layer 9 444 is extremely high compared to the rest of the sequence while  $\delta^{13}C_{\text{shell}}$  and the Sr/Ca 445 446 ratio decrease in this layer pointing to less arid conditions. However, these data 447 correspond to a single fragment from a layer with a small archaeological sample, 448 typical of a transient camp used for specific activities. Hence, we discuss the 449 palaeoclimatic information from this component mostly based on layer 10 data. 450 It could be interpreted that small groups of hunter-gatherers from the eastern 451 steppe used rocky shelters like PDC in the area of LAM as temporal camps, possibly 452 logistically integrated from base camps described by other researchers to the eastern 453 steppe (Crivelli Montero 2010), including transitional sectors of cypress forests in 454 Valle Encantado (Hajduk and Albornoz 1999; Hajduk et al. 2011) and some 455 occupations of forested sites in the Traful area (Silveira 1996, 1999). This would 456 have been favored by arid conditions that had changed part of the forest area and 457 related wetlands into grasslands suitable for grazing by steppe herbivores, especially 458 guanacos, which do not tolerate wet soils. Additionally, these incursions could have 459 also been related to the gathering of obsidian from sources located in the forest area 460 near the MAL. This is supported by the presence of obsidian characterized by the 461 same chemical groups and tools with similar laminarity as those found in PDC in 462 steppe sites (Pérez et al. 2019). This occupation may have not persisted as a result of 463 climate changes not recorded because of the absence of shell remains in the hiatus 464 between the Lower and Middle components and/or because the rock detachment 465 from the cave's walls made this site not suitable for human use.

In the Middle component, the three analyzed proxies are mostly coincident.  $\delta^{18}O_{shell}$ shows low values with a negative peak in layer 7 (Fig. 5), which could indicate a long humid period (lower effect of evaporation on  $\delta^{18}O_{water}$ ). Sr/Ca ratio is also low in layers 6 and 7, with the negative peak in the same layer as  $\delta^{18}O_{shell}$ , reinforcing the idea of a wet period with high river discharge, at least in layers 6 and 7. Records of  $\delta^{13}C_{shell}$  are slightly lower in this component than in the others in layer 8 and show a marked

472 negative peak in layer 6, suggesting higher input of forest-derived organic matter and 473 soil alkalinity due to increased runoff. Terrestrial plant material can provide low  $\delta^{13}$ C organic compounds, which would be reflected in  $\delta^{13}C_{shell}$  through deposition of 474 475 metabolic C in shell carbonate (Gajurel et al. 2006; see McConnaughy and Gillikin 2008, for a review). In turn, soil derived alkalinity contributes with low  $\delta^{13}$ C HCO<sub>3</sub><sup>-</sup>, 476 477 which is the main source of shell carbonate (e.g. Leng and Marshall 2004). Taken 478 together, the three analyzed proxies reflect high humidity and high river discharge in the 479 middle component (990-1050 AD), especially in layers 6 and 7. The fact that the amplitude of the changes in  $\delta^{18}O_{shell}$  is lower than that of the other proxies could 480 indicate that this period was also cold, since  $\delta^{18}O_{\text{shell}}$  in *D. chilensis* increases as 481 482 temperature decreases (Soldati et al. 2009), which would partially counteract the effect 483 of the humid conditions. Villalba (1990, 1994) has previously reported a cold humid 484 period (900 - 1070 AD) in the same region based on alerce tree rings, while Moy et al. 485 (2008) have interpreted positive moisture balance between 850 and 1100 AD from  $\delta^{18}$ O 486 records on *Pisidum sp.* valves and on the fine fraction of Lago Guanaco sediments in 487 the Southern Chilean Patagonia.

488 At the time corresponding to the Middle component of PDC, hunter-gatherer 489 populations from South-Central Chile, which possessed a complex economy, including 490 pottery, fishing, incipient agriculture, and common burial grounds (Aldunate 1989; 491 Dillehay 1990; Adán et al. 2016; Campbell et al. 2018) began to colonize this area, 492 possibly as a result of the temporary segmentation of large groups, including a more 493 recurrent occupation of the eastern side of the Andes (Aldunate 1989; Pérez 2010. The 494 increased precipitation rate suggested by the proxies analyzed above is 495 contemporaneous with an increase in the intensity of SWW that was reported to occur 496 in several areas of Southern Patagonia (e.g. Echeverría et al. 2017). The climatic models 497 for Patagonia predict a strong positive effect of SWW on precipitations on the West side 498 of the Andes, which becomes weaker on the East side forest area and neutral to negative 499 in the forest-steppe ecotone and in the steppe, respectively (Kilian and Lamy 2012; 500 Garreaud et al. 2013). Thus, these human groups from the western side of the Andes 501 could have increased their residential mobility towards the Eastern forest and the 502 neighbor ecotone during the time of precipitation peaks. This geographic expansion 503 could also be partly related to brief abrupt climate changes, accompanied by volcanic 504 episodes and forest fires, which have been reported for the west side of the Andes range 505 during this period (Pérez 2010). In general, the precipitation peaks, volcanic activity

episodes and fires were short duration catastrophic events, which were recurrent in this period and favored the fragmentation of large groups and their mobilization to more benign areas as an adaptive response (Jones et al. 1999). These were short-term responses and the groups returned to their original location when the extreme events were over. Accordingly, Torrence (2002) has proposed a response to volcanic episodes of short duration in New Guinea, with human groups migrating to unaffected areas and returning to the original area when conditions were favorable again.

The archaeological evidence in the Middle component suggests the recurrent occupation of MAL by people with forest adaptations in the form of short-term camps both, under rocky shelters and in open sites. These groups interacted with the local environment and made intensive use of the local resources, as is detailed in 1.3, but no changes in their way of life or technology are evident from the quality of the artifacts recovered, which does not change throughout the record of this component (Pérez 2010; Pérez et al. 2017).

520 The Upper component (layers 5-1) is partially contemporaneous with a warm and 521 dry period between 1080 and 1250 AD, reported by Villalba (1990; 1994) as an 522 expression of the MCA in the area of Los Alerces National Park, North-West 523 Patagonia (Figs. 1,5) and with a period of high evaporation in Lago Guanaco (Moy et 524 al. 2008). In this component,  $\delta^{18}O_{shell}$  starts to rise in layer 5 and is high throughout 525 the component except for a negative peak in layer 4, which does not correlate with 526 the values of the other proxies. If this negative peak is excluded, pooled  $\delta^{18}O_{shell}$  in 527 this component is significantly higher than in the Middle component (Student's t test, p < 0.05). Similarly,  $\delta^{13}C_{\text{shell}}$  is significantly higher in the upper than in the middle 528 529 component, considering all the layers (Student's t test, p < 0.05), and the Sr/Ca ratio 530 is consistently high between layers 4 and 1. Although Sr/Ca ratio remains low as in 531 the middle component in layer 5, this value is not correlated with the other two 532 proxies.

In layer 3, which coincides with the highest level of occupation of the MAL, all the three proxies considered in this discussion are consistent at maximum values, pointing to a dry-warm climate with high aquatic plants productivity. This result is in agreement with the conditions described by Villalba (1990; 1994) for the same period (Fig. 5). From the archaeological analysis, this layer seems to be an occupation floor, in which the maximum human activity for this site can be inferred from a high artifact deposition rate (Pérez 2011). According to the artifactual

540 evidence, at this time, the PDC occupants remained in the site for several decades 541 (Pérez 2010, Pérez et al. 2019). Layer 2 is contemporary with a cold period thought 542 by Villalba (1990; 1994) to be a local expression of the Little Ice Age. Although we 543 have recorded slight changes in  $\delta^{13}C_{\text{shell}}$  and in Sr/Ca ratio with respect to layer 3, 544  $\delta^{18}O_{\text{shell}}$  does not change. Thus, no clear evidence pointing to the expression of the 545 Little Ice Age in the area of MAL can be observed in the sequence studied in this 546 work.

547 The Upper component shows a new colonization event after a period of no or 548 scarce occupation of the area. The reoccupation of the MAL included potentially 549 articulated camps in open sites and rocky shelters made by the same populations 550 which had temporarily expanded their mobility during the Middle component. In this 551 component, the increment in residential mobility occurred in the context of a new 552 stage of colonization (Borrero 1994-1995). At variance with the Middle component, 553 this mobility was not correlated with environmental instability but with increasing 554 aridity.

This climatic event persisted for many decades, enabling the effective occupation 555 556 of the territory (Borrero 1994-1995). The relatively stable environmental conditions 557 recorded between layers 5 and 1 have probably favored the intensification, in this 558 case, related to an evident increase in the interaction with the local resources, with 559 predominant use of local raw materials, such as obsidian and clay. This would have 560 also stimulated changes in the organization of various cultural aspects (Jones et al. 561 1999), including the production of large combustion structures related to the local 562 production of pottery described by Pérez (2011) and technological innovations, such 563 as lithic sinkers for fishing lines and new shapes in the projectile points (Pérez et al. 564 2017).

565 The resulting capacity to exploit local resources may have allowed these groups to 566 cope with the increasing aridity recorded from layer 5, with peak in layer 3 by taking 567 advantage of the increased aquatic productivity. For this period, previous papers 568 describe an active exchange of resources and technology among populations of the 569 Pacific coast, the Central valleys of Chile and the Argentine side of the Andes Range 570 (Aldunate 1989; Pérez 2010; Campbell et al. 2018), similar to the described by 571 Arnold (1992) for island and inland populations of California and Santa Barbara 572 channel, in the Northern hemisphere.

573

574 4 CONCLUSIONS

Journal Pre-proof

575 We have reconstructed a palaeoclimatic multiproxy sequence based on stable 576 isotopes and trace metals measured in archaeological D. chilensis shell remains, 577 which allows to correlate the sequence of human occupations of the MAL with 578 environmental changes at a resolution scale with no antecedents for this region. We 579 have detected climatic change pulses and the local expression of climatic events, 580 such as the MCA, which have previously been registered for only one site in North 581 Patagonia, which covers an area with a radius of 100 km. (Villalba, 1990, 1994). Our 582 results allow to extend the geographic area in which the expression of the MCA is 583 evident in North Patagonia by ca. 300 km to the North and could contribute to the 584 development of regional interpretations. Since D. chilensis is one of the most 585 abundant species in the archaeofauna of a wide region comprising North-West 586 Patagonia, Argentina and South-Central Chile, this multi-proxy approach is a 587 promising tool for the interpretation of landscapes and climates in which human 588 populations migrated into and developed in the past. 589 Goñi et al. (2019) proposed that in Austral Patagonia, the climatic fluctuations 590 occurred along the last 2500 years, especially the MCA and other events caused the 591 reduction of the residential mobility of hunter-gatherer groups of the Center-West of 592 Santa Cruz province (Fig. 1). In contrast, we have identified palaeoenvironmental 593 trends, which can be associated with changes in mobility, technology and use of 594 natural resources in the MAL by human populations with different ways of life and 595 territoriality. The occupations of the area occur when it becomes comparatively 596 advantageous relative to the areas occupied by different human populations. For 597 example, the archaeological remains found in the Lower component of PDC suggest

exploratory incursions from the Eastern steppe, mostly related with the gathering of
lithic raw materials and favored by arid conditions in the forest area, which extended
the steppe herbivores distribution range towards the forest-steppe ecotone, ca. 2.300
BP.

In the last millennium, when the MAL became advantageous relative to the West side of the Andes, it was colonized and effectively occupied by populations from South-Central Chile, which possessed an efficient technology for exploiting forest and freshwater resources. The first colonization by these groups, with recurrent short-term occupations, took place during a humid period with high precipitation rates and environmental instability (ca.990-1080 A.D) related to increased intensity

- 608 in the SWW. This effect was milder in the Eastern slopes of the Andes, where the 609 influence of the SWW is less important than in the Western side. The second, and 610 more permanent occupation by the same groups was contemporary with the local 611 expression of the MCA (ca. 1080 and 1250 AD), and was probably favored by 612 increased productivity of the rivers and lakes. Besides, the effective occupation with 613 increasing degree of interaction with the local resources from the lower to the upper 614 component was stimulated by the longer duration of the favorable environmental 615 conditions. 616 Finally, the MAL record allows us to propose that the different models that
- 617 suggest social complexity, mobility, resource intensification and territorial behavior
- 618 during moments of environmental instability associated to the MCA are probably not
- 619 monothetic and / or contradictory, but rather they can be complementary and / or
- 620 concurrent.
- 621

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906	Captions to the figures
907	Figure 1. Meliquina Archaeological Locality (MAL, 1) including the Parque Diana
908	Cave (PDC) and associated open (Meliquina Lake) sites, and related steppe sites (3, 4),
909	in North-West Patagonia, Argentina. The location of MAL (1) and reference sites for
910	paleoclimatic reconstruction in North-West (2) and Austral (5) Patagonia are shown in a
911	regional map. SWW, South Westerly Winds.
912	
913	Figure 2. A- Excavation in Parque Diana Cave showing part of the cave's
914	wall. B- South profile and layer 10 (Lower component) C- Planimetry of the
915	three components showing the distribution of the archaeological remains.
916	
917	Fig.3. Stratigraphic sequence at the Parque Diana Cave consisting of
918	thirteen 10 cm thick layers pooled into three cultural components.
919	Left, East profile of the cave; center, percentage of recovered Diplodon
920	<i>chilensis</i> shells per layer; right, <sup>14</sup> C chronology.
921	
922	Fig.4. Diplodon chilensis shells collected from the different layers of
923	Parque Diana Cave.
924	
925	Figure 5. Stable isotope ratios (V-PDB ‰, right y axis) and element/Ca ratios (mg/g,
926	left y axis) recorded in shell carbonates of Diplodon chilensis from the stratigraphic
927	sequence of Parque Diana Cave. $\delta^{18}O$ (open triangles) and $\delta^{13}C$ (closed triangles)
928	data are plotted as mean, $n = 3$ for layers 2, 3, 6 and 10, $n = 2$ for layer 8 and $n = 1$
929	for layers 1, 4, 5, 7 and 9. Sr/Ca and Mn/Ca ratios are represented by open and closed
930	circles, respectively, $n = 1$ . The human activities interpreted from the archaeological
931	record of the Parque Diana Cave are shown below the graph. The arrow indicates the
932	expression of the Medieval Climatic Anomaly (MCA) in the same region, according
933	to Villalba (1990; 1994).
934	

- 936 Table 1. pH, Number of identified specimens (NISP) and fragmentation
- 937 index (F.I.) in the 10 layers of the site Parque Diana cave which contained
- 938 Diplodon chilensis shell remains.
- 939

Layer	pН	NISP	F.I
1	7.58	10	0.20
2	7.69	52	0.30
3	7.32	77	0.26
4	7.91	10	0.36
5	7.71	4	0.25
6	7.78	3	0.33
7	7.73	5	0.20
8	7.56	4	0.25
9	7.64	1	0.00
10	7.29	2	0.50

940

941

942 Table 2. Element concentrations measured by TXRF in Río Hermoso water

943	and in	the	shells	of	living	Dip	lodon	chilens	is.
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	Ca	Mn	Sr	Fe	Zn
Water (µg/mL)	5.695	0.012	0.031	0.113	0.044
Shell (mg/g)	216.3	0.168	1.144	1.308	0.428

- 946 **APPENDIX A** 947 Antecedents of paleoenvironmental reconstruction using stable isotopes and trace 948 elements, with emphasis on freshwater bivalves' shells. 949 950 **Stable isotopes** 951 Stable isotopes, especially those of oxygen (18O) and carbon (13C), have been widely 952 used as proxies for palaeoclimate reconstruction since the early works by McCrea 953 (1950) and Epstein et al. (1953). For this purpose, isotopic ratios, e.g. 180/160, are 954 expressed in delta notation (e.g.  $\delta$ 18O) relative to internationally accepted standards. 955  $\delta$ 18O palaeothermometry is based on the principle that if carbonates (or phosphates) 956 precipitate in equilibrium with the surrounding water, the isotopic ratio in the mineral 957 depends only on water isotopic ratio and precipitation temperature. Thus, if water  $\delta 180$ 958 is known, temperature can be estimated from the carbonate  $\delta 180$  (reviewed in 959 Grossman 2012). 960 Stable isotopes have been recorded in samples from great variety of biogenic materials, 961 such as carbonates from foraminifers and limpet shells (e.g. Barker et al. 2005; 962 Ferguson et al. 2011), carbonates or phosphates from fossil groups like branchiopods, 963 belemnites and conodonts (Grossman 2012), phosphates and collagen from extinct 964 mammals (e.g. González Guarda et al. 2017), and cellulose from tree rings (Lavergne et 965 al. 2017). 966 Bivalve mollusks are especially good candidates for palaeoclimate reconstruction since 967 they deposit carbonate in equilibrium with ambient water, their shells present 968 conspicuous annual growth lines, and are relatively well preserved through time. 969 Particularly,  $\delta$ 18Oshell is closely related to the host water isotopic composition and 970 temperature (Carre et al. 2005; Dettman et al. 1999; Epstein et al. 1953; Ferguson et al. 971 2011; Gordillo et al. 2015; Grossman and Ku 1986; Grossman 2012; McCrea 1950; Yan
- 972 et al. 2009; Yoshimura et al. 2010.
- 973 Valve growth, structure, mineralogy, and isotopic and chemical fractionation, can be
- 974 affected by variations in environmental parameters, such as water isotopic composition,
- 975 temperature, food supply, type of substrate, salinity, dissolved oxygen concentration or
- 976 oxygen/carbon ratio. Thus, shell isotopic patterns or signs can serve as archives of
- environmental history (Dettman et al. 1999; Gajurel et al. 2006; Goodwin et al. 2003;
- 978 Kaandorp et al. 2003; Schöne et al. 2007).
- 979 Freshwater bivalves

Hydrological and climate conditions such as river discharge and the balance between 980 981 precipitation and evaporation can also be principal factors affecting  $\delta$ 180water and thus 982 δ18Oshell. (Gajurel et al. 2006; Kaandorp et al. 2003; 2006; Marwick and Gagan 2011; 983 Ricken et al. 2003; Rodrigues et al. 2000; Schöll-Barna 2011; Versteegh et al. 2010; 984 2011). Carbon isotopic ratio ( $\delta$ 13Cshell) can covariate with  $\delta$ 18Oshell and has also 985 been discussed in previous papers as an isotopic proxy for reconstruction of marine 986 palaeoenvironments (e.g. Surge and Walker 2006). In freshwater environments, 987  $\delta$ 13Cshell can be affected by biological factors, which modify the proportion of 988 metabolic C deposited in the shell and by many environmental factors such as 989 temperature, evaporation, soil derived dissolved carbon and the kind and productivity of 990 the dominant plants (or phytoplankton) (Geist et al. 2005; Gillikin et al. 2009; Goewert 991 et al. 2007; Goodwin et al. 2012; Kaandorp et al. 2003; Keller et al. 2002; Klein et al. 992 1996; Krantz et al. 1987; Leng and Marshall 2004; Lorrain et al. 2004; McConnaughey 993 and Gillikin 2008; Moy et al. 2008; Surge and Walker 2006).

994

#### 995 Trace elements

Since different divalent cations can substitute for calcium in biogenic carbonates, their 996 997 presence in carbonate deposits or in the shells of aquatic species has been widely 998 studied as proxies for environmental reconstruction. According to Barker et al. (2005), 999 trace element ratios can be analyzed in parallel with  $\delta$ 180 measured in the same sample 1000 for obtaining more robust temperature estimations. For marine mollusks, Ferguson et al. 1001 (2011) report that both Mg/Ca ratio and  $\delta$ 18O in modern shells of limpets (Patella spp.) 1002 reflect the seasonal regime of surface seawater temperature (SST) of the western 1003 Mediterranean. In contrast, Füllenbach et al. (2015) argue that the incorporation of Sr 1004 and Mg is often strongly controlled by physiological factors, and thus Sr/Ca and Mg/Ca 1005 ratios are not reliable as palaeothermometers.

1006 Besides their relative suitability for palaeothermometry, trace elements can supply

1007 information about past environmental conditions, since shell element/Ca ratios reflect

- 1008 the concentration of elements, such as Mn and Sr in the ambient water at the time of
- 1009 calcification (Carroll and Romanek 2008; Jeffree et al. 1995). Peacock and Seltzer
- 1010 (2008) have recorded increased Sr/Ca ratio in bivalve shells from the late Holocene and
- 1011 discussed such results in terms of aridity, while Kaandorp et al. (2006) have correlated
- 1012 Sr concentration in bivalve shells with precipitation-evaporation cycles in Amazonian
- 1013 freshwaters. Besides water chemistry, temperature, soil erosion, primary productivity

- 1014 and processes associated with growth exert strong controls on the incorporation of trace
- 1015 elements, together with other physiological factors which can vary among different
- 1016 species (Carré et al. 2006; Carroll and Romanek 2008; Freitas et al. 2006; Füllenbach et
- 1017 al. 2015; Klein et al. 1996; Langlet et al. 2007; Lazaret et al. 2003; Takesue and van
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Dr. Thijs van Kolfschoten Editor Quaternary International

Dear Dr. Kolfschoten,

None of the authors have any conflicts of interest to declare.

Kind regards

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