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Stable isotopes ($\delta^{13}\text{C}$, $\delta^{18}\text{O}$) and element ratios (Mg/Ca, Sr/Ca) of Jurassic belemnites, bivalves and brachiopods from the Neuquén

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1 **Stable isotopes ($\delta^{13}\text{C}$, $\delta^{18}\text{O}$) and element ratios (Mg/Ca, Sr/Ca) of Jurassic belemnites,**
2 **bivalves, and brachiopods from the Neuquén Basin (Argentina): challenges and**
3 **opportunities for palaeoenvironmental reconstructions**

4
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23
24 **Abstract:** Fossils from the Jurassic succession of the Neuquén Basin (Argentina) were
25 analysed for their stable isotope ($\delta^{13}\text{C}$, $\delta^{18}\text{O}$) and elemental (Mg/Ca, Sr/Ca) composition.
26 Mg/Ca ratios point to comparatively stable temperature conditions from the Bajocian to Early
27 Oxfordian and during the Tithonian, but do not allow a reliable reconstruction of absolute
28 water temperatures. Sr/Ca ratios follow the general global pattern indicating water exchange
29 between the basin and the open ocean. The $\delta^{18}\text{O}$ values can be translated into water
30 temperatures between 20 to 25 °C for most of the studied intervals with possible shorter cold
31 spells in the Late Pliensbachian, Bajocian, and Late Tithonian. However, precise temperature
32 reconstructions are complicated by bivalve shells from the northern/central part of the basin
33 pointing to local fluctuations in the $\delta^{18}\text{O}$ values of seawater. Potential reasons for these
34 variations are discussed, but it seems most likely that they are caused by phases of enhanced

35 freshwater input leading to meso- to brachyhaline conditions in the northern study areas. The
36 present article therefore exemplifies the particular challenges for temperature reconstructions
37 in marginal seas and highlights the opportunities of combining different geochemical proxies
38 to disentangle the influence of different environmental parameters.

39

40 **Keywords:** Jurassic, Argentina, Neuquén Basin, geochemistry, temperatures, palaeoclimate.

41

42 Over the last decades, stable oxygen isotope analyses of fossil hardparts ($\delta^{18}\text{O}_{\text{shell}}$) were used
43 to continuously improve our understanding of the Jurassic world and climate (e.g., Bowen,
44 1963; Stevens and Clayton, 1971; Ditchfield et al., 1994; Price and Sellwood, 1997; Dromart
45 et al., 2003; Dera et al., 2011; Korte et al., 2015). Nevertheless, such studies focusing mainly
46 on the reconstruction of water temperatures are still dominated by data for European localities
47 with other regions being comparatively understudied. In order to differentiate between global
48 and regional trends, data from other regions are necessary. The present study concentrates on
49 the Jurassic of Argentina and is part of a series of articles aimed at deepening our
50 understanding of environmental conditions of Gondwanan localities (Alberti et al., 2012a, b,
51 2013, 2017, 2019a, b, 2020).

52 South America has extensive Jurassic successions, which have been studied by
53 geoscientists for considerable time (e.g., pioneer studies by Steuer, 1897; Burckhardt, 1900,
54 1903; Haupt, 1907; Weaver, 1931). Their rich fossil content has sparked various
55 palaeontological studies and also allowed the establishment of a biostratigraphic framework
56 based on ammonites with an ever-increasing resolution. Although well-preserved fossils are
57 common in many stratigraphic intervals, attempts at reconstructing environmental conditions
58 during the Jurassic based on geochemical analyses of well-dated shells are still few (e.g.,
59 Bowen, 1963; Volkheimer et al., 2008; Gómez-Dacal et al., 2018; Alberti et al., 2019b).
60 Temperature reconstructions based on $\delta^{18}\text{O}_{\text{shell}}$ analyses in particular necessitate assumptions
61 on the depositional setting including water depth or the $\delta^{18}\text{O}$ value of seawater ($\delta^{18}\text{O}_{\text{sea}}$)
62 during the life time of the analysed fossil organisms. Influences such as evaporation, river
63 discharge, or rainfall patterns are particularly important for marginal seas such as the
64 Neuquén Basin, which was separated from the open ocean by a volcanic arc (Fig. 1; compare
65 Lazo et al., 2008). In order to differentiate environmental parameters, the present study
66 combines the analyses of stable isotopes ($\delta^{18}\text{O}$, $\delta^{13}\text{C}$) and element ratios (Mg/Ca, Sr/Ca) of
67 179 fossil specimens from the Neuquén Basin. Elemental analyses (Fe, Mn) were also used to
68 evaluate the preservational quality of the studied fossils.

69

70 **Geological overview**

71

72 The Neuquén Basin is situated between 34-41° S and 66-71° W in southwestern South
73 America covering approximately 120,000 km² of present-day Chile and Argentina (Fig. 2;
74 Howell et al., 2005; Parent et al., 2013). The Triassic-Paleogene succession consists of several
75 thousand metres of sedimentary rocks including an almost complete Jurassic-Early
76 Cretaceous marine record (Howell et al., 2005). During most of its development and until
77 today, the Neuquén Basin was delimited by the Sierra Pintada Massif in the northeast and the
78 North Patagonian Massif in the south, while the Andean volcanic arc separated the basin from
79 the open Pacific Ocean (Fig. 1). It is unknown to which degree water exchange with the open
80 ocean was possible or where exactly seaways for such an exchange existed. Some
81 reconstructions depict the volcanic arc as a loose chain of islands (e.g., Howell et al., 2005;
82 Fig. 1A). In contrast, Vicente (2005) proposed a more restricted situation with a single
83 connection north of the basin (i.e. the Curepto Strait; Fig. 1B). Eventually, the continued
84 Andean orogeny led to the uplift and folding of the Mesozoic strata, which became
85 subsequently exposed in the western part of the Neuquén Basin (Howell et al., 2005).

86 The material used in the present study has been collected from two groups of outcrops:
87 (1) the northern sections in the vicinity of Chos Malal and (2) the southern sections near
88 Zapala (Fig. 2). The two areas are approximately 180 km apart and characterized by slightly
89 different depositional settings (Fig. 3). The northern sections near Chos Malal include the
90 localities of Vega de la Veranada (VV) and Pampa Tril (PT). Studied outcrops in this area
91 include Bajocian to lower Cretaceous rocks with marine fossils occurring at several levels. In
92 the Bathonian to Oxfordian strata, bivalves occur regularly, while belemnites and ammonites
93 become more common in the Tithonian. Ammonites allow precise age assignments for large
94 parts of the succession (compare Parent and Garrido, 2015; Parent et al., 2015, 2020). In
95 general, siliciclastic rocks (partly cross-bedded) dominate the Middle Jurassic, but the Upper
96 Callovian to Oxfordian La Manga Formation is characterized by carbonates interpreted as a
97 distal platform (Gulisano, 1992). The Middle Oxfordian to Kimmeridgian strata consist of
98 massive evaporites and continental rocks. The Tithonian to lowermost Cretaceous units are
99 again dominated by fine-grained siliciclastics which were interpreted as basinal to outer ramp
100 deposits (e.g., Spalletti et al., 1999). Finally, the Lower Valanginian Mulichinco Formation
101 consists of calcareous sandstones with oysters (Schwarz and Howell, 2005).

102 The following sections were sampled near Zapala in the southern Neuquén Basin:
103 Portada Covunco (PC), Cerrito Caracoles (CC), Cerro Granito (CG), Picún Leufú (PL-1&2),
104 Picún Leufú Campamento Vialidad (PL-CV), and Charahuilla (CH). Some of these localities
105 represent classic sections studied since many decades (e.g., Suero, 1951; Westermann and
106 Riccardi, 1979; Leanza, 1990, 1993; Leanza et al., 2013). In general, the depositional setting
107 in the southern Neuquén Basin has been described as more shallow than further north due to
108 the Huincul Arch (compare Parent et al., 2013). Consequently, the fossil fauna is often more
109 diverse including bivalves, ammonites, brachiopods, gastropods, echinoderms, hermatypic
110 corals, and serpulids (e.g. Armella et al., 2007, 2008; Garrido and Parent, 2013; Parent et al.,
111 2013). The succession is dominated by marine siliciclastics with intercalations of continental
112 rocks (e.g., in the Callovian and Kimmeridgian; Fig. 3). A noteworthy exception is the
113 Tithonian Picún Leufú Formation, which consists of bioclastic limestones in addition to
114 calcareous siltstones. The individual localities and sections are described in more detail in the
115 Supplementary Material (including geographic coordinates and information on
116 biostratigraphy).

117

118 **Material and methods**

119

120 In total, 119 bivalves, 50 belemnites, seven brachiopods, and three aptychi were analysed in
121 the present study (for photographs of exemplary specimens see the Supplementary Material).
122 Most of these fossils were collected during a field survey in February 2018 at the localities of
123 Vega de la Veranada, Pampa Tril, and Picún Leufú 1. Additional shells were selected from
124 the collections of the Museo Provincial de Ciencias Naturales “Prof. Dr. Juan A. Olsacher” in
125 Zapala, Argentina. The vast majority of the selected shells are oysters belonging to the genus
126 *Gryphaea*. In addition, few shells of *Actinostreon*, *Aetostreon*, *Placunopsis*, and *Trichites*
127 were analysed (Aberhan, 1994; Rubilar, 2005; Lazo, 2007; Rubilar and Lazo, 2009; Bressan
128 and Palma, 2010). Jurassic belemnites of the Neuquén Basin are still relatively poorly known.
129 The majority of the Bajocian rostra have a short conical form without a groove and could be
130 assigned to the genus *Brevibelus*. The Callovian-Oxfordian specimens are characterized by a
131 depressed cross-section with a prominent ventral groove and can be assigned to the genus
132 *Belemnopsis*. The Tithonian belemnites belonging to the genus *Hibolites* show mostly
133 elongate rostra, which are cylindrical in cross-section and have no or only a weak shallow
134 ventral groove (Howlett, 1989; Doyle, 1992; Doyle et al., 1996, 1997). Analysed brachiopods
135 were identified as the rhynchonellid species *Rhynchonelloides lamberti*, *Piarorhynchia*

136 *keideli*, and *Rhynchonella variabilis*. Due to occasional fragmentary preservation, not all
137 collected fossils could be identified to generic level.

138 Most of the collected fossils can be attributed to a particular horizon and ammonite
139 zone in already previously published sections (see Supplementary Material for details). The
140 individual sections were correlated based on regional and Tethyan ammonite biostratigraphy
141 and "theoretical" absolute ages were assigned to each sample based on the Geological Time
142 Scale 2016 (Ogg et al., 2016). This age model is theoretical in the extent that dating and
143 correlating of ammonite zones in South America are on-going processes and continuous
144 changes are expected in the future (e.g., Lena et al., 2019). Even though such changes and
145 improvements in dating might change the assigned absolute ages of the samples, the overall
146 trends discussed in the present study will likely remain the same. The northern sections near
147 Chos Malal are represented with samples from the Lower-Middle Bathonian to Lower
148 Oxfordian and the Tithonian. Fossils of the southern sections near Zapala were collected from
149 the Pliensbachian, Lower Bajocian, Bathonian, and Tithonian. The sampling focus lay on
150 Middle and Upper Jurassic sections, but no fossils could be collected from the Middle
151 Oxfordian to Kimmeridgian interval, as the corresponding strata consist of continental to
152 evaporitic deposits, which do not contain marine fossils (Fig. 3).

153 The collected fossils were examined macroscopically and the seemingly best
154 preserved specimens were subsequently cleaned and sampled with a hand-held dental drill.
155 For bivalves and brachiopods, the areas close to the umbo/hinge and near muscle scars were
156 avoided, since these are often influenced by vital effects during shell formation (e.g.,
157 Carpenter and Lohmann, 1995). Similarly, belemnite rostra were not sampled close to the
158 outer rim or near the alveole, since these are commonly prone to alteration. Large oyster
159 shells were rare, but one specimen of *Gryphaea* sp. from the Lower Oxfordian could be cut
160 longitudinally and sampled at high-resolution with 27 samples taken along a transect
161 perpendicular to the growth lines. In addition, five samples of sediment and one sample of
162 cement filling the alveole of a belemnite rostrum were collected. All specimens are
163 permanently stored at the Museo Provincial de Ciencias Naturales "Prof. Dr. Juan A.
164 Olsacher" in Zapala, Argentina.

165 The collected carbonate powder was analysed using a carbonate preparation device
166 (Kiel IV) connected to a ThermoScientific MAT 253 mass spectrometer at the Leibniz
167 Laboratory for Radiometric Dating and Stable Isotope Research at the Christian-Albrechts-
168 Universität zu Kiel, Germany. The carbonate samples were reacted within the preparation
169 device with 100 % orthophosphoric acid at 75 °C and the evolved CO₂ gas was then analysed

170 using the mass spectrometer. On daily routine, different laboratory internal carbonate
171 standards and two international carbonate standards (NBS-19; IAEA-603) were analysed to
172 control the precision of measured $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ values. All values are reported in per mil
173 relative to the Vienna Pee Dee Belemnite (VPDB) scale using NBS-19. Analytical precision
174 of stable isotope analysis was better than $\pm 0.08\text{‰}$ ($\pm 1\text{SD}$) for $\delta^{18}\text{O}$ and better than $\pm 0.05\text{‰}$
175 ($\pm 1\text{SD}$) for $\delta^{13}\text{C}$.

176 In most cases, the sample size was large enough for elemental analyses in addition to
177 stable isotope analyses. Samples were dissolved in dilute nitric acid and analysed for their
178 Mg/Ca and Sr/Ca ratios and Fe, Mn mass fractions using an ICP-OES instrument (Spectro
179 Ciros SOP) at the Institut für Geowissenschaften, Christian-Albrechts-Universität zu Kiel,
180 Germany. Average uncertainty for Sr/Ca was around 0.9‰ and for Mg/Ca around 1.2‰.
181 Reference materials Coral JcP-1, Tridacna JcT-1, and carbonate ECRM 752 were used as
182 secondary standards.

183 Within the present study, potential correlations between different analytical results in
184 the acquired datasets were evaluated with the help of the Spearman correlation coefficient
185 (r_s). Illustrated linear trend lines are based on reduced major axis (RMA) regression.

186

187 **Results**

188

189 Detailed results of the geochemical analyses are listed in the Supplementary Material.

190

191 *Preservation of the fossil material*

192

193 A thorough check of the preservational quality is very important in any study using fossil
194 shells for geochemical analyses. Cathodoluminescence microscopy has become a standard
195 procedure to examine whether diagenetic alteration changed the chemical composition of
196 fossil shells (e.g., Wierzbowski, 2002, 2004; Wierzbowski and Joachimski, 2007; Ullmann
197 and Korte, 2015; Arabas, 2016; Arabas et al., 2017), but unfortunately such an easy check
198 was not possible in the current study since the fossil material had to remain in Argentina.
199 Instead, iron and manganese contents were analysed for most of the used specimens, which
200 also allow an evaluation of preservational quality (e.g., Brand and Veizer, 1980, 1981; Price
201 and Sellwood, 1997; Wierzbowski and Joachimski, 2007; Wierzbowski et al., 2009; Fujioka
202 et al., 2019). Since concentrations of both elements are relatively low in pristine shells, cut-off
203 values can be defined which may be used to separate potentially altered samples from the

204 database. Results from sediment and cement samples show high iron and manganese contents,
205 thereby attesting to the availability of both elements in pore waters. Consequently, all fossils
206 with an iron content above 300 $\mu\text{g/g}$ and a manganese content above 100 $\mu\text{g/g}$ were removed
207 from environmental reconstructions (compare similar cut-off values used by Wierzbowski and
208 Joachimski, 2007; Wierzbowski et al., 2009; Nunn and Price, 2010; Alberti et al., 2012b;
209 Arabas et al., 2017). Furthermore, all specimens for which elemental analysis could not be
210 performed were considered unreliable and excluded from further interpretations. Of the 119
211 sampled bivalves, twelve did not yield enough carbonate powder for elemental analysis and
212 47 were deemed unreliable because of exceeding the cut-off grades in their iron and/or
213 manganese content. This left 60 presumably well-preserved bivalve shells. Of the 50 sampled
214 belemnite rostra, 48 could be analysed for their element content. Five belemnite rostra were
215 removed from further interpretations due to high iron and/or manganese contents. This left 43
216 seemingly well-preserved belemnites. Most of the collected brachiopods showed some
217 abrasion on the outer shell surface. Due to their thin inner shell layer, only two of the seven
218 brachiopod shells yielded enough sample material for elemental analyses and both were
219 considered well-preserved. Finally, all three aptychi were deemed unreliable since their data
220 reflect either diagenetically altered carbonate or contamination by carbonate cements filling
221 the abundant pores in the shell plates. After elemental analyses, the collection was separated
222 into seemingly well-preserved specimens and possibly unreliable fossils. While both datasets
223 are included in the Supplementary Material, only results of the well-preserved fossils were
224 used for interpretations.

225 Another potential indicator for the alteration of the stable isotope composition of fossil
226 shells is a correlation of their $\delta^{18}\text{O}$ and $\delta^{13}\text{C}$ values (e.g., Hodgson, 1966; Ullmann and Korte,
227 2015). Even though such a correlation can occasionally be primary in origin (e.g., due to a
228 stronger primary productivity at higher temperatures), diagenetic alteration commonly leads
229 to a decrease in $\delta^{18}\text{O}$ and $\delta^{13}\text{C}$ values (e.g., Hodgson, 1966; Hudson, 1977; Nelson and Smith,
230 1996). This can be demonstrated by the results from the sediment samples, which show much
231 lower $\delta^{18}\text{O}$ and $\delta^{13}\text{C}$ values than well-preserved fossils. Similarly, several fossil shells, which
232 were considered unreliable and potentially diagenetically altered because of their high iron
233 and/or manganese contents, exhibit lowered $\delta^{18}\text{O}$ and $\delta^{13}\text{C}$ values (Fig. 4). Consequently, an
234 increasing alteration of shells should lead to a positive correlation between the stable isotope
235 values. In contrast, the 60 well-preserved bivalve shells show a negative correlation ($r_s =$
236 -0.60 , $p < 0.05$) which is believed to be caused by the strong variation of analytical results
237 between the different study areas instead of diagenetic alteration. If only the bivalves of the

238 northern sections are considered, the negative correlation is weaker ($r_s = -0.44$, $p < 0.05$; Fig.
239 4). The oysters of the southern sections show no significant correlation ($r_s = -0.16$, $p = 0.58$;
240 Fig. 4). Similarly, the $\delta^{18}\text{O}$ and $\delta^{13}\text{C}$ values of the 43 well-preserved belemnites show no
241 significant correlation ($r_s = 0.00$, $p = 0.97$; Fig. 4), also if separated by study area.

242

243 *Results of stable isotope and trace element analyses*

244

245 Since the results are markedly different between the northern and the southern sections, both
246 will be described separately in the following paragraphs.

247

248 Northern sections near Chos Malal. The $\delta^{13}\text{C}$ values of well-preserved oyster shells near Chos
249 Malal (Fig. 5A) show an increase from the Early-Middle Bathonian (average: 2.09 ‰) to the
250 Late Callovian (Dimorphosus Zone, average: 3.83 ‰) and then a slight decrease into the
251 Early Oxfordian (Pressulus Zone, average: 3.31 ‰). No samples are available from the
252 Kimmeridgian, but in the Early Tithonian $\delta^{13}\text{C}$ values are low (Picunleufuense Zone, average:
253 0.91 ‰). Values then increase slightly towards the Middle Tithonian (Zitteli/Mendozanus
254 Zone, average: 1.74 ‰) and then decrease again until the Late Tithonian (Alternans Zone,
255 minimum: -0.33 ‰). The two oyster shells with a Valanginian age have again slightly higher
256 $\delta^{13}\text{C}$ values (Riveroi Zone, average: 1.10 ‰). The number of belemnites from the northern
257 sections is comparatively limited, but the results show a similar pattern to the oysters with
258 higher $\delta^{13}\text{C}$ values in the Early Oxfordian (Pressulus Zone, average: 0.57 ‰) and lower
259 values in the Tithonian (average: -1.11 ‰).

260 The $\delta^{18}\text{O}$ values of well-preserved Jurassic oyster shells of the northern sections (Fig.
261 5B) are all strikingly low (below -5 ‰). The data show a gradual increase from the Early-
262 Middle Bathonian (average: -8.59 ‰) to the Early Oxfordian (Pressulus Zone, average: -7.54
263 ‰). After a gap in data, this trend can be followed further from the Early Tithonian
264 (Picunleufuense Zone, average: -6.45 ‰) to the Late Tithonian (Alternans Zone, maximum:
265 -5.11 ‰). The two Valanginian oysters show much higher $\delta^{18}\text{O}$ values (Riveroi Zone,
266 average: -2.66 ‰). In contrast to the oysters, the belemnites of the northern sections show no
267 characteristic trend through time, but much higher absolute values. In the Early Oxfordian
268 (Pressulus Zone), $\delta^{18}\text{O}$ values of belemnites vary around an average of -0.67 ‰. In the
269 Tithonian, values are again a bit lower (average: -1.59 ‰) but also quite scattered (between
270 -4.20 and -0.40 ‰).

271 The Mg/Ca ratios of well-preserved oysters of the northern sections remain largely
272 stable through time (Fig. 5C). The record begins in the Early-Middle Bathonian (average:
273 2.42 mmol/mol) and changes little until the Early Oxfordian (Pressulus Zone, average: 2.36
274 mmol/mol). Values are similar in the Early (Picunleufuense Zone, average: 2.85 mmol/mol)
275 and Middle Tithonian (Zitteli/Mendozanus Zone, average: 2.13 mmol/mol; Internispinosum
276 Zone, average: 2.90 mmol/mol). Mg/Ca-ratios in the Late Tithonian (Alternans Zone)
277 fluctuate mostly around an average of 1.63 mmol/mol, except for one outlier with a Mg/Ca
278 ratio of 8.16 mmol/mol (sample MOZ-PI 11834/1). The two oysters from the Valanginian
279 (Riveroi Zone) have Mg/Ca ratios around an average of 2.51 mmol/mol. In comparison, the
280 belemnites have much higher Mg/Ca ratios. The two specimens of the Early Oxfordian
281 (Pressulus Zone) have values around an average of 8.52 mmol/mol. In the Tithonian, the
282 ratios fluctuate strongly around an average of 11.35 mmol/mol (between 7.92 and 14.42
283 mmol/mol).

284 The Sr/Ca ratios of oyster shells (Fig. 5D) of the northern sections are relatively stable
285 from the Early-Middle Bathonian (average: 0.59 mmol/mol) to the early Late Callovian
286 (Primus Zone, average: 0.60 mmol/mol). Following this, the Sr/Ca ratio decreases and reaches
287 lowest values in the Early Oxfordian (Pressulus Zone, average: 0.46 mmol/mol). In the
288 Tithonian, Sr/Ca ratios are generally higher and show an increase from the Early Tithonian
289 (Picunleufuense Zone, average: 0.75 mmol/mol) to the Middle Tithonian (Zitteli/Mendozanus
290 Zone, average: 1.07 mmol/mol) and a subsequent decrease until the Late Tithonian (Alternans
291 Zone, minimum: 0.73 mmol/mol). The two Valanginian (Riveroi Zone) oysters show Sr/Ca
292 ratios around an average of 0.86 mmol/mol. The Sr/Ca ratios of belemnites of the Early
293 Oxfordian (Pressulus Zone) vary around an average of 1.39 mmol/mol. In the Tithonian, the
294 values fluctuate more strongly around an average of 1.78 mmol/mol (between 1.33 and 2.17
295 mmol/mol).

296
297 Southern sections near Zapala. Two well-preserved rhynchonellid brachiopod shells with a
298 Pliensbachian age show $\delta^{13}\text{C}$ values around an average of 3.96 ‰ (Fig. 6A). A well-preserved
299 Early Bajocian (Giebeli Zone) oyster shell has a $\delta^{13}\text{C}$ value of 3.70 ‰ (sample MOZ-PI
300 11830/1) and another oyster shell from the Bathonian has a $\delta^{13}\text{C}$ value of 3.35 ‰ (sample
301 MOZ-PI 11254). Considerably more data is available from well-preserved oyster shells with a
302 Late Tithonian (Alternans Zone) age, which show $\delta^{13}\text{C}$ values around an average of 0.61 ‰.
303 Even though the dataset is limited (especially for the Bajocian and Bathonian), the values
304 seem to show an overall decrease in $\delta^{13}\text{C}$ values from the Middle to Late Jurassic, similar to

305 the northern sections (Fig. 5A). In addition, the recorded absolute $\delta^{13}\text{C}$ values of oyster shells
306 are similar between the northern and southern sections (particularly for the Late Tithonian
307 where more data is available for both areas). The 34 well-preserved belemnites with an Early
308 Bajocian age (Giebeli Zone) show $\delta^{13}\text{C}$ values between 0.55 and 3.04 ‰ (average: 1.69 ‰).

309 The $\delta^{18}\text{O}$ record starts with two rhynchonellid brachiopods of Pliensbachian age with
310 values ranging around an average of -3.24 ‰ (Fig. 6B). Two well-preserved oysters from the
311 Middle Jurassic give $\delta^{18}\text{O}$ values of -1.44 ‰ for the Early Bajocian (Giebeli Zone) and -3.08
312 ‰ for the Bathonian. The $\delta^{18}\text{O}$ values of oysters from the Late Tithonian (Alternans Zone)
313 fluctuate around an average of -1.47 ‰. These values are much higher than those recorded
314 from oysters of the northern sections. Furthermore, they do not show a very prominent trend
315 through time. Belemnites of the Early Bajocian (Giebeli Zone) recorded $\delta^{18}\text{O}$ values between
316 -1.52 and -0.16 ‰, except for one outlier with -3.19 ‰. Their overall average is -0.81 ‰,
317 which is largely comparable to values of belemnites from the northern sections, even though
318 the latter have different ages.

319 The two brachiopods with a Pliensbachian age recorded Mg/Ca ratios with an average
320 of 4.83 mmol/mol (Fig. 6C). The Mg/Ca ratios of well-preserved oysters are slightly lower
321 but relatively stable through time. The oyster shells from the Early Bajocian (Giebeli Zone)
322 and the Bathonian show Mg/Ca ratios of 2.10 and 2.41 mmol/mol respectively. In the Late
323 Tithonian (Alternans Zone), Mg/Ca ratios of well-preserved oysters vary around an average of
324 2.91 mmol/mol. In general, the results are similar to those of oysters from the northern
325 sections in absolute values and by being relatively stable through time. The belemnites with
326 an Early Bajocian age (Giebeli Zone) show much higher Mg/Ca ratios around an average of
327 12.80 mmol/mol (ranging between 7.80 and 17.10 mmol/mol).

328 The two Pliensbachian brachiopod shells show Sr/Ca ratios around an average of 1.08
329 mmol/mol (Fig. 6D). The Sr/Ca ratios of well-preserved oyster shells seem relatively constant
330 through time. Oysters from the Early Bajocian (Giebeli Zone) and the Bathonian have Sr/Ca
331 ratios of around 0.72 mmol/mol. The Sr/Ca ratios of well-preserved bivalve shells from the
332 Late Tithonian (Alternans Zone) fluctuate around an average of 0.71 mmol/mol. The
333 belemnites with an Early Bajocian age (Giebeli Zone) have Sr/Ca ratios around an average of
334 1.58 mmol/mol (ranging between 1.38 and 1.80 mmol/mol).

335

336 *Results of the high-resolution stable isotope analysis*

337

338 One oyster shell (*Gryphaea* sp.) from the Lower Oxfordian (Pressulus Zone) of the Vega de la
339 Veranada has been sampled at high-resolution across growth layers approximately 1 cm
340 below the umbo (Fig. 7; Supplementary Material). A total of 27 samples was taken with an
341 average resolution of three samples per millimeter. These samples were analysed for their
342 stable isotope composition. The $\delta^{18}\text{O}$ values show a cyclic nature around an average value of
343 -7.06‰ with a maximum at -5.77‰ and a minimum at -8.33‰ (Fig. 7A). There are a total
344 of three (possibly four) cycles visible in the $\delta^{18}\text{O}$ values with the amplitude becoming
345 increasingly weaker towards the younger side of the shell. The $\delta^{13}\text{C}$ values fluctuate less
346 strongly around an average of 3.45‰ (maximum: 3.79‰ ; minimum: 3.09‰ ; Fig. 7B). They
347 show a broad positive excursion in the older half of the shell and a broad negative excursion
348 in the younger half. Overall, the $\delta^{18}\text{O}$ and $\delta^{13}\text{C}$ values show a weak correlation ($r_s = 0.45$; $p =$
349 0.02 ; Fig. 7C).

350

351 **Discussion**

352

353 *Differences between water temperature proxies*

354

355 Several geochemical methods have been developed and applied to reconstruct absolute water
356 temperatures in Earth's history including the Jurassic (e.g., Urey et al., 1951; Epstein et al.,
357 1951; McArthur et al., 2007; Jenkyns et al., 2012; Li et al., 2013; Wierzbowski et al., 2018;
358 Vickers et al., 2019). Among these, stable isotope ($\delta^{18}\text{O}_{\text{shell}}$) analysis has certainly become the
359 most commonly used procedure leading to fundamental improvements of our understanding
360 of the climate development in the Jurassic (e.g., Dera et al., 2011; Martinez and Dera, 2015;
361 Korte et al., 2015). While results for different benthic taxa (e.g., bivalves and rhynchonellid
362 brachiopods) are generally similar (e.g., Alberti et al., 2012a), belemnite rostra have often
363 been found to record higher $\delta^{18}\text{O}_{\text{shell}}$ values than co-occurring benthic organisms (e.g.,
364 Prokoph et al., 2008; Mutterlose et al., 2010; Alberti et al., 2012a, 2019a). When using the
365 same method for temperature reconstructions, this difference leads to the reconstruction of
366 water temperatures commonly 4-5 °C lower for belemnites compared to shells of co-occurring
367 bivalves or rhynchonellid brachiopods (also compare Dera et al., 2011). A series of reasons
368 has been suggested for this seemingly systematic difference, including different life habits
369 (e.g., a migratory behavior of belemnites) or vital effects during the formation of the
370 belemnite rostrum (e.g., Mutterlose et al., 2010; Hoffmann and Stevens, 2019). Since
371 belemnites are an extinct faunal group, deciphering all processes affecting the stable isotope

372 composition of their hardparts is difficult. In any case, it is clear that results from belemnites
373 should be interpreted cautiously and separately from those of benthic organisms. For Jurassic
374 calcitic shells, absolute palaeotemperatures are most commonly calculated by the equation
375 given by Anderson and Arthur (1983) with a $\delta^{18}\text{O}_{\text{sea}}$ value of -1‰ during shell formation (as
376 suggested for an ice-free world; Shackleton and Kennett, 1975). Following this approach,
377 stable isotope analyses for belemnite rostra of the northern and southern sections as well as
378 for the oysters and brachiopods of the southern sections lead to reasonable water temperatures
379 (Figs 5, 6). Oxfordian and Tithonian belemnites from the northern sections show a slightly
380 higher variation indicating water temperatures between 13.1 and 20.5 °C with an outlier at
381 30.6 °C (overall average: 17.8 °C). The Bajocian belemnites of the southern sections indicate
382 water temperatures between 12.6 and 18.2 °C with one outlier at 25.7 °C (overall average:
383 15.2 °C). As expected, the $\delta^{18}\text{O}_{\text{shell}}$ values of oysters and brachiopods of the southern sections
384 would translate into slightly higher temperatures between 16.6 and 27.0 °C (average: 19.4
385 °C). In contrast, the oysters of the northern sections near Chos Malal recorded $\delta^{18}\text{O}_{\text{shell}}$ values
386 below -5‰ , which would correspond to unrealistic temperatures of 35 to 60 °C.

387 Reconstructing absolute water temperatures based on several different element ratios
388 has become another standard method (particularly using foraminifers and corals; e.g., Eggins
389 et al., 2003; Corrège, 2006; McArthur et al., 2007; Cléroux et al., 2008; Hetzinger et al., 2016;
390 Pfeiffer et al., 2017). Experiments on recent bivalve shells have shown that Mg/Ca ratios
391 indeed reflect water temperatures and might be more independent of freshwater influence or
392 enhanced evaporation compared to $\delta^{18}\text{O}_{\text{shell}}$ values (e.g., Klein et al., 1996; Bougeois et al.,
393 2016). However, these studies also revealed that the exact relationship between water
394 temperature and Mg/Ca ratio in the shell depends strongly on the examined species.
395 Consequently, different equations for temperature reconstructions have been developed for
396 different taxa (compare Surge and Lohmann, 2008; Nunn and Price, 2010; Mouchi et al.,
397 2013; Tynan et al., 2017). Since the species used in the current study are long extinct, their
398 Mg/Ca-temperature relationship cannot be measured anymore. Consequently, all temperature
399 reconstructions based on Mg/Ca ratios of extinct organisms should be treated cautiously.
400 Nevertheless, even though absolute temperature estimates based on Mg/Ca ratios might be
401 unreliable, temperature trends through time might be captured with this method.

402 Belemnites, which do not have closely related, living relatives are especially difficult
403 to interpret. Nunn and Price (2010) proposed an equation to translate Mg/Ca ratios of
404 belemnite rostra into water temperatures. Using their equation, the Oxfordian and Tithonian
405 specimens of the northern sections would indicate water temperatures between 17.2 and 23.3

406 °C (average: 19.6 °C; Fig. 5C), values that are in the same range of those estimated from
407 $\delta^{18}\text{O}_{\text{shell}}$ values. Similarly, the Bajocian specimens of the southern sections would translate
408 into temperatures between 17.0 and 24.2 °C (average: 21.4 °C; Fig. 6C). However, whether
409 the Mg/Ca ratios of belemnite rostra can be used for temperature reconstructions is still
410 debated. While authors such as Nunn and Price (2010) have found a negative correlation
411 between Mg/Ca ratios and $\delta^{18}\text{O}_{\text{shell}}$ values in belemnites and assumed that temperatures
412 determine the oxygen isotope and Mg/Ca ratio in the rostra (sometimes also Sr/Ca; e.g.,
413 McArthur et al., 2007), Li et al. (2013) have found no such correlation in their analyses of
414 Jurassic and Cretaceous belemnites and concluded that this ratio is unreliable as a palaeo-
415 temperature proxy. In the current dataset, there is a weak negative correlation between
416 $\delta^{18}\text{O}_{\text{shell}}$ values and Mg/Ca ratios of belemnites, whether examined for the entire collection (rs
417 = -0.35, p = 0.02) or separately for specimens of the north (rs = -0.68, p = 0.05) and south (rs
418 = -0.32, p = 0.07). At the same time, there is no correlation between $\delta^{18}\text{O}_{\text{shell}}$ values and Sr/Ca
419 ratios of belemnites (rs = -0.04, p = 0.82; compare Supplementary Material).

420 If the equation developed by Mouchi et al. (2013) for modern, juvenile *Crassostrea*
421 *gigas* is used for the Jurassic oysters of the Neuquén Basin, their Mg/Ca ratios translate into
422 relatively cool water temperatures. The Mg/Ca ratios of the oyster shells of the northern
423 sections do not vary much from the Bathonian up until the Tithonian (Fig. 5C) and would
424 indicate temperatures between 7.6 and 15.1 °C with one outlier of 32.6 °C in the Late
425 Tithonian (overall average: 11.5 °C). Similarly, the oysters of the southern sections show
426 relatively little variation in their Mg/Ca ratios, which would translate into temperatures
427 between 6.4 and 18.0 °C (average: 12.5 °C). However, these absolute temperature values
428 depend very strongly on the used equation and there is no reason to assume that the equation
429 of Mouchi et al. (2013) applies to the presently used Jurassic species. Nevertheless, another
430 equation developed by Surge and Lohmann (2008) for the modern *Crassostrea virginica* in an
431 estuarine setting leads to even colder temperatures, if applied to the present dataset. In any
432 case, it should be noted that the Mg/Ca ratios are more or less the same for material from the
433 northern and southern sections.

434 In summary, it seems that $\delta^{18}\text{O}_{\text{shell}}$ values of rhynchonellid brachiopods and oysters
435 allow the most reliable and realistic absolute water temperature reconstructions, if the $\delta^{18}\text{O}_{\text{sea}}$
436 value can be approximated properly. In contrast, the $\delta^{18}\text{O}_{\text{shell}}$ values of belemnite rostra lead to
437 an underestimation of water temperatures if following the traditional approach by using the
438 equation of Anderson and Arthur (1983) or require the usage of a separate equation difficult

439 to establish for this extinct group. Finally, Mg/Ca ratios are strongly dependent on species-
440 specific fractionation factors.

441

442 *The Sr/Ca ratio of seawater*

443

444 Previous authors proposed that Sr/Ca ratios of fossil hardparts reflect ancient water
445 temperatures based on a negative correlation with $\delta^{18}\text{O}_{\text{shell}}$ values (compare McArthur et al.,
446 2007; Sosdian et al., 2012). However, subsequent research failed to confirm a strong link
447 between water temperatures and Sr/Ca ratios (Korte and Hesselbo, 2011). Similarly, the
448 present dataset from Argentina shows no correlation between Sr/Ca ratios and $\delta^{18}\text{O}_{\text{shell}}$ values.
449 Instead it seems that the ratio is largely a function of species-specific factors (e.g.,
450 fractionation factor, metabolism) and the original Sr/Ca ratio of the surrounding water body
451 (compare Steuber and Veizer, 2002; Ullmann et al., 2013). Ullmann et al. (2013)
452 reconstructed Sr/Ca ratios of Jurassic seawater by using a Sr distribution coefficient of 0.10
453 for bivalve shells and a coefficient of 0.32 for belemnite rostra. If these coefficients are
454 applied on the current dataset of the Neuquén Basin, the results of the northern and southern
455 sections are similar (Fig. 8) and compare well to the proposed global seawater Sr/Ca curve
456 compiled from data of Ullmann et al. (2013, 2016). The results of the two Pliensbachian
457 brachiopod shells are also comparable with the global curve if a Sr distribution coefficient of
458 0.32 is used. The most striking features of the curve of Ullmann et al. (2013, 2016) are a
459 decrease in seawater Sr/Ca ratios throughout the Middle Jurassic, a minimum in the
460 Oxfordian, a subsequent increase in values towards the mid-Tithonian, and a slight decrease
461 again towards the Jurassic-Cretaceous boundary. This trend is attributed to global tectonic
462 events (Ullmann et al., 2013) and is also similar to the global $^{87}\text{Sr}/^{86}\text{Sr}$ curve as compiled by
463 McArthur et al. (2012) and Wierzbowski et al. (2017). While both proxies do not have to be
464 directly related, Ullmann et al. (2013) suggested a common cause for the parallel fluctuations
465 in an interplay between continental input and mid-ocean ridge activity. In any case, the
466 current data suggest that water exchange between the Neuquén Basin and the open ocean
467 occurred during the sampled time intervals, even though both were separated by a volcanic
468 arc (Fig. 1). The slightly higher absolute values could be explained by uncertainties in the Sr
469 distribution coefficients for the used fossil taxa. Alternatively, an influx of water masses with
470 higher Sr/Ca ratios into the basin has to be postulated. In general, modern rivers have Sr/Ca
471 ratios lower than those of modern oceans (e.g., Sosdian et al., 2012) except for some arid

472 regions in which riverine Sr/Ca ratios can be up to 16.0 mmol/mol (Holmden and Hudson,
473 2003).

474

475 *The $\delta^{18}\text{O}$ value of seawater*

476

477 Reconstructions of absolute water temperatures based on $\delta^{18}\text{O}_{\text{shell}}$ values of fossil hardparts
478 require knowledge of the $\delta^{18}\text{O}_{\text{sea}}$ value. Most studies focusing on the Jurassic time interval use
479 a $\delta^{18}\text{O}_{\text{sea}}$ value of -1‰ to acknowledge the lack of polar ice shields (Shackleton and Kennett,
480 1975). In general, this is an oversimplification which neglects a likely latitudinal gradient in
481 $\delta^{18}\text{O}_{\text{sea}}$ values, with considerably higher values in the tropics and lower values at high
482 latitudes, caused by the hydrological cycle (compare Zachos et al., 1994; Roche et al., 2006;
483 LeGrande and Schmidt, 2006). However, the Neuquén Basin was situated at a palaeolatitude
484 of ca. 40° S throughout most of the Jurassic (Besse and Courtillot, 2002; Torsvik et al., 2012;
485 van Hinsbergen et al., 2015), which corresponds approximately to the point where the
486 latitudinal $\delta^{18}\text{O}_{\text{sea}}$ gradient could have reached the value -1‰ (compare Alberti et al., 2020).
487 Thus, using this value in the equation of Anderson and Arthur (1983) leads to the
488 reconstruction of reasonable water temperatures for the studied well-preserved belemnites, as
489 well as the oyster and brachiopod shells of the southern sections. In contrast, the $\delta^{18}\text{O}_{\text{shell}}$
490 values of the bivalves from the northern sections are very negative and would correspond to
491 very high, unrealistic water temperatures. Several options are theoretically possible to explain
492 such negative $\delta^{18}\text{O}_{\text{shell}}$ values, which will be discussed in the following (compare Fig. 9).

493 (1) Possibly the simplest explanation for very negative $\delta^{18}\text{O}_{\text{shell}}$ values in any fossil
494 record is a poor preservation of the analysed specimens, since diagenetic alteration generally
495 leads to a shift of $\delta^{18}\text{O}_{\text{shell}}$ values to more negative values. However, as described above, no
496 signs of pronounced alteration are present in the used oyster shells. Furthermore, the presence
497 of cyclic changes in $\delta^{18}\text{O}_{\text{shell}}$ values in the oyster used for high-resolution stable isotope
498 analysis (Fig. 7) does not support strong diagenetic alteration, which would have most likely
499 led to a more uniform stable isotope composition throughout the shell. Consequently,
500 alteration seems to be an unlikely cause for the documented negative $\delta^{18}\text{O}_{\text{shell}}$ values of
501 bivalves from the northern sections.

502 (2) If diagenetic alteration is ruled out as a possible factor and average water
503 temperatures between 20 to 25 °C are assumed for the Middle to Late Jurassic, the very
504 negative $\delta^{18}\text{O}_{\text{shell}}$ values would correspond to $\delta^{18}\text{O}_{\text{sea}}$ values at the northern study areas (=
505 northern/central Neuquén Basin) of -7 to -6‰ in the Bathonian to Early Oxfordian and -5 to

506 -4‰ in the Tithonian. Such low $\delta^{18}\text{O}_{\text{sea}}$ values characterize polar waters, which are
507 commonly enriched in ^{16}O (e.g., $\delta^{18}\text{O}_{\text{sea}}$ values of -5‰ and below have been recorded in
508 present-day high latitudes and it can be assumed that similar and lower values were possible
509 in the Jurassic; Schmidt et al., 1999; Thomas and Mol, 2018). Theoretically, north-bound
510 currents along the South American west coast could have transported polar ocean waters
511 northwards during the Jurassic (similar to today). However, the Neuquén Basin was situated
512 at a palaeolatitude of 40° S during the Middle and Late Jurassic and it seems unlikely that
513 ocean currents could transport a negative $\delta^{18}\text{O}_{\text{sea}}$ signal so far to the north. In fact, models for
514 absolute $\delta^{18}\text{O}_{\text{sea}}$ values in the Cretaceous do not predict particularly low values at comparable
515 latitudes in the southern hemisphere (Zhou et al., 2008). Danise et al. (2020) described the
516 Jurassic temperature development of the Sundance Seaway of northwestern North America.
517 In this region (at a palaeolatitude of ca. 40° N), Middle Jurassic oysters with very negative
518 $\delta^{18}\text{O}_{\text{shell}}$ values were explained by an influx of Arctic waters into the epicontinental basin. The
519 palaeogeography of the Sundance Seaway with only one connection to the open ocean at high
520 latitudes in northern North America is relatively well known. In contrast, it is still debated to
521 which extent the volcanic arc separated the Neuquén Basin from the open ocean (Fig. 1).
522 Some palaeogeographic reconstructions indicate a rather loose chain of islands, which would
523 allow water exchange through a series of channels west of the actual basin (e.g., Spalletti et
524 al., 2000: fig. 8; Howell et al., 2005: fig. 4). Similarly, the Sr/Ca ratios measured for the
525 current study point to water exchange with the open ocean during the studied time intervals
526 (see above). In contrast, Scherer and Goldberg (2007: fig. 1) seem to imply that the main
527 connection to the open ocean was situated at high latitudes in southern South America.
528 However, if an influx of polar waters from the south into an otherwise restricted Neuquén
529 Basin is used to explain the very negative $\delta^{18}\text{O}_{\text{shell}}$ values of the oysters from the northern
530 sections, it seems unclear, why the remaining fossils do not show similar values. Furthermore,
531 Vicente (2005: fig. 13; 2006) proposed that the major connection of the Neuquén Basin with
532 the open ocean was actually situated in the north (i.e. the Curepto Strait; Fig. 2B) and the
533 basin might have been closed towards the south (also compare Howell et al., 2005: fig. 4;
534 Parent, 2006; Kietzmann et al., 2014: fig. 1; Godoy, 2015: fig. 2). It might be speculated that
535 upwelling along the South American west coast could bring polar water masses with low
536 $\delta^{18}\text{O}_{\text{sea}}$ values into the Neuquén Basin. While seasonal upwelling along western South
537 America has been predicted by some Jurassic climate models (Price et al., 1995), no evidence
538 for this process has been found yet in sediments, fossil faunas, or geochemistry (e.g., Li
539 enrichments in shells; Sadatzki et al., 2019).

540 (3) The formation of sea ice leads to water masses with higher salinities and lower
541 $\delta^{18}\text{O}_{\text{sea}}$ values that sink to the sea floor (compare Barrera et al., 1987; Ravelo and Hillaire-
542 Marcel, 2007). However, at a palaeolatitude of 40° S for the Neuquén Basin in the Middle and
543 Late Jurassic, the formation of extensive sea ice is very unlikely (even though some Jurassic
544 climate models suggest sub-zero temperatures at comparable palaeolatitudes in India;
545 Sellwood et al., 2000). Furthermore, changes in $\delta^{18}\text{O}_{\text{sea}}$ values via sea ice formation would
546 only be seasonal.

547 (4) The breakdown of volcanoclastics into smectite and mixed layer clays at the
548 sediment-water interface and/or within the sediment can lower $\delta^{18}\text{O}$ values by several per mil
549 in bottom and pore waters (Lawrence et al., 1979; Price and Sellwood, 1997). The existence
550 of an active volcanic arc allowed a continuous supply of volcanoclastics into the Neuquén
551 Basin. However, it is not clear why this process should only affect the northern study areas.
552 Furthermore, this geochemical process alone is not strong enough to cause the proposed
553 negative $\delta^{18}\text{O}_{\text{sea}}$ values.

554 (5) Freshwater is generally enriched in ^{16}O and commonly used to explain negative
555 $\delta^{18}\text{O}_{\text{sea}}$ values. River discharge or strong rainfalls modify $\delta^{18}\text{O}_{\text{sea}}$ values particularly in surface
556 waters, because freshwater forms lenses on top of the heavier saline water. Such freshwater
557 influence restricted to the northern study areas could explain the very negative $\delta^{18}\text{O}_{\text{shell}}$ values
558 of the bivalves. Meso- to brachyhaline conditions (salinities 16-20) in the Bathonian, Late
559 Callovian, and Early Oxfordian would correspond to $\delta^{18}\text{O}_{\text{sea}}$ values of -7 to -6 ‰ at average
560 water temperatures of 20°C (based on the method of Lazo et al., 2008: fig. 3). The proposed
561 $\delta^{18}\text{O}_{\text{sea}}$ values of -5 to -4 ‰ for the Tithonian would correspond to brachyhaline conditions
562 (salinities 23-27). While oysters are generally tolerant towards fluctuations in salinities and
563 live in marine as well as brackish habitats, ammonites and belemnites are considered
564 stenohaline. However, since these cephalopods are active swimmers, they might have
565 migrated throughout the basin and did not necessarily live within the presumably brackish
566 waters in the northern study areas. Separate habitats would explain the higher $\delta^{18}\text{O}_{\text{shell}}$ values
567 of the belemnites from the northern sections. Post-mortem drift of cephalopod shells over
568 wide distances is also not unlikely.

569 Climate models for the Jurassic of South America predict the position of the
570 Intertropical Convergence Zone (ITCZ) towards the north of the Neuquén Basin (Scherer and
571 Goldberg, 2007). While the area of the basin itself was situated in a dry region (e.g.,
572 Volkheimer et al., 2008), rainfalls towards the north of the basin might have occurred
573 regularly and fueled rivers draining into the northern Neuquén Basin. Since palaeolatitudes

574 did not change markedly during the Middle and Late Jurassic, such a situation might have
575 been stable for long time intervals. Because very low $\delta^{18}\text{O}$ values are limited to the northern
576 sections, this area might have been more restricted than the southern part. This is supported by
577 the presence of two thick evaporitic units in the northern/central Neuquén Basin (Fig. 3).
578 During these phases, the Curepto Strait must have been closed (as suggested by Vicente,
579 2005) and the northern basin was thus separated from the open ocean (due to sea-level
580 changes and local tectonic movements; Hallam, 2001). Lazo et al. (2008; see also Aguirre-
581 Urreta et al., 2008) studied the stable oxygen isotope composition of Early Cretaceous oysters
582 in the northern/central Neuquén Basin north of Zapala and near Chos Malal. Similar to the
583 Jurassic data from this study, their results include very negative $\delta^{18}\text{O}_{\text{shell}}$ values. The authors
584 explained these values by freshwater influence in the basin during certain intervals in the
585 Cretaceous. It seems therefore reasonable to propose salinity fluctuations in the sampled
586 northern/central Neuquén Basin throughout the Jurassic and Cretaceous as a result of an
587 interplay between changing river influx and sea water exchange leading either to brackish
588 conditions or the formation of evaporites. Such a scenario changes the general understanding
589 of the northern/central Neuquén Basin somewhat as this area was originally considered to
590 represent a more distal and deeper area. Even though the Tithonian is dominated by fine-
591 grained sediments possibly deposited below wave base, the Bathonian to Oxfordian strata
592 sampled here commonly show cross-bedded horizons, which cannot be deposited at high
593 water depths. Interestingly, the $\delta^{18}\text{O}_{\text{shell}}$ values of bivalves are less negative in the Tithonian
594 compared to the Bathonian to Oxfordian, possibly indicating a weaker freshwater influence
595 towards the end of the Jurassic, when sea level was generally higher.

596

597 *Seasonal temperature changes*

598

599 The Lower Oxfordian oyster used for high-resolution analysis shows a cyclic signal in its
600 $\delta^{18}\text{O}_{\text{shell}}$ values interpreted to reflect seasonal patterns. However, as in other shells from the
601 northern sections, the $\delta^{18}\text{O}_{\text{shell}}$ values are very low. Using a $\delta^{18}\text{O}_{\text{sea}}$ value of -1‰ , the $\delta^{18}\text{O}_{\text{shell}}$
602 data would translate into unrealistic temperatures between 39 and 53 °C (Fig. 7A). On the
603 other hand, the shell's Mg/Ca ratio would indicate an unrealistically low temperature of 12.5
604 °C by using the equation of Mouchi et al. (2013). If a $\delta^{18}\text{O}_{\text{sea}}$ value of -6.5‰ is applied
605 accounting for the proposed freshwater influence, a seasonality of about 11 °C is
606 reconstructed (minimum: 13.0 °C, maximum: 24.0 °C; Fig. 7A). Due to the problems in
607 reconstructing precise $\delta^{18}\text{O}_{\text{sea}}$ values, these absolute temperatures are less reliable. However,

608 the temperature amplitude (= seasonality) might be in fact a reasonable estimate for the
609 Neuquén Basin in the Oxfordian at a palaeolatitude of 40° S. In addition, fossils analysed in
610 the present study and collected from one stratigraphic interval show a comparable variation,
611 possibly reflecting a similarly strong seasonality (also compare ranges in results of Bowen,
612 1963). Nevertheless, additional seasonal fluctuations in the $\delta^{18}\text{O}_{\text{sea}}$ values caused, for
613 example, by seasonal rainfall cannot be excluded completely. In addition, the cyclic nature of
614 the $\delta^{18}\text{O}_{\text{shell}}$ data of the oyster from Vega de la Veranada shows that the northern study areas
615 were at least occasionally shallow enough to experience seasonal environmental changes (i.e.,
616 above the thermocline).

617

618 *A synopsis on Jurassic water temperatures of South America*

619

620 So far, reconstructions of absolute water temperatures for the southern hemisphere in the
621 Jurassic are comparatively few in number. Figure 10 combines Jurassic temperature data from
622 South America including the present dataset from the Neuquén Basin as well as results of
623 Bowen (1963), Gómez-Dacal et al. (2018), and Alberti et al. (2019b).

624 Mg/Ca ratios of oysters and belemnites of the Neuquén Basin do not allow the reliable
625 reconstruction of absolute water temperatures, but point to more or less stable temperature
626 conditions throughout the studied Middle to Late Jurassic intervals. Pliensbachian
627 brachiopods show higher Mg/Ca ratios than Bajocian and Bathonian oysters, but since the
628 relationship between the Mg/Ca ratio and temperature differs strongly between species, it is
629 not clear whether this decrease in values reflects a temperature decrease (Fig. 10A).

630 The Jurassic stable oxygen isotope record of South America (Fig. 10B) starts with data
631 from Chile published recently by Alberti et al. (2019b). While fossils near Potrerillos in
632 northern Chile show possible freshwater influence, the specimens analysed from sections
633 around El Transito likely recorded water temperatures (compare Alberti et al., 2019b). These
634 shells indicate temperatures around an average of 25.9 °C in the Late Sinemurian, identical to
635 the average of 25.9 °C recorded by the two Pliensbachian brachiopods of the Neuquén Basin.
636 One brachiopod from the latest Pliensbachian of Chile might reflect the likely global Late
637 Pliensbachian Cooling Event with a comparatively low temperature of 19.6 °C (compare
638 Alberti et al., 2019b). Late Toarcian temperatures of Chile are again relatively high around an
639 average of 24.4 °C based on brachiopod and bivalve shells. Bowen (1963) analysed seven
640 seemingly well-preserved, but poorly dated belemnite rostra of the late Early Jurassic. A total
641 of thirty $\delta^{18}\text{O}_{\text{shell}}$ values from the seven fossils translate into water temperatures between 12.4

642 and 25.3 °C. The poor stratigraphic resolution somehow diminishes the value of these
643 temperature reconstructions. The Middle Jurassic record starts with one Bajocian oyster of the
644 Neuquén Basin, which recorded a relatively low temperature of 17.8 °C. Another oyster from
645 the Bathonian shows again a higher temperature of 25.2 °C. Middle to Late Jurassic
646 belemnites of the Neuquén Basin analysed in the present study indicate relatively constant
647 water temperatures around averages of 15.2 °C for the Early Bajocian, 14.6 °C for the Early
648 Oxfordian, and 18.7 °C for the Tithonian. These values are largely comparable to results of
649 Bowen (1963), who analysed eight samples of two belemnite rostra from the Middle Bajocian
650 with reconstructed temperatures between 14.4 and 23.4 °C. As discussed above, $\delta^{18}\text{O}_{\text{shell}}$
651 values of the oysters from the northern sections point to a change in $\delta^{18}\text{O}_{\text{sea}}$ values in this area,
652 possibly caused by enhanced freshwater influence. If water temperatures between 20 and 25
653 °C are assumed, then a $\delta^{18}\text{O}_{\text{sea}}$ value of -6.5 ‰ for the Bathonian to Early Oxfordian and -4.5
654 ‰ for the Tithonian can be proposed (Fig. 10B). While $\delta^{18}\text{O}_{\text{shell}}$ values of these oysters can
655 therefore not be used to reconstruct reliable water temperatures, the stability of Mg/Ca ratios
656 throughout this time interval suggests the absence of major temperature changes. Oyster shells
657 from the southern sections recorded water temperatures around 18.0 °C in the Late Tithonian,
658 before temperatures increase again into the Valanginian (Early Cretaceous) with two oysters
659 pointing to temperatures around 23.2 °C. Gómez-Dacal et al. (2018) analysed Tithonian to
660 Valanginian oyster shells from three sections in the northern/central Neuquén Basin with
661 results matching the present data comparatively well (Fig. 10B). Tithonian oysters of Gómez-
662 Dacal et al. (2018) show a wide variability in $\delta^{18}\text{O}_{\text{shell}}$ values translating into water
663 temperatures between 20.0 and 33.4 °C (for a $\delta^{18}\text{O}_{\text{sea}}$ value of -1 ‰), possibly reflecting
664 freshwater influence on some of the shells. During the Berriasian, reconstructed water
665 temperatures are more confined around an average of 23.2 °C, but in the Early Valanginian
666 values are again quite scattered (between 21.5 and 31.7 °C). These scattered values might
667 indicate that freshwater influx in the northern/central Neuquén Basin occurred also in the
668 Early Cretaceous. Such a scenario is also supported by Lazo et al. (2008) who recorded
669 several intervals with very negative $\delta^{18}\text{O}_{\text{shell}}$ values of oysters in the Valanginian to Barremian
670 of the northern/central Neuquén Basin and postulated lowered salinities in this area.

671

672 *Other Jurassic water temperature records of the southern hemisphere*

673

674 Apart from South America, research on Jurassic water temperatures at comparatively high
675 southern latitudes has focused on James Ross Island in Antarctica, New Zealand, and the
676 Malvinas (Falkland) Plateau.

677 Ditchfield et al. (1994) analysed Jurassic and Cretaceous macrofossils from James
678 Ross Island in Antarctica. Their collection included ammonites, belemnites, and bivalves with
679 a Tithonian age. Of these, eight belemnite rostra were considered to be well-preserved and
680 yielded $\delta^{18}\text{O}_{\text{shell}}$ values between -1.20 and -0.26 ‰, corresponding to water temperatures of
681 16.8 to 13.0 °C. Ditchfield et al. (1994) mentioned a palaeolatitude of around 60° S for the
682 James Ross Island, but newer reconstructions point to a palaeolatitude of 45 - 50° S (van
683 Hinsbergen et al., 2015).

684 Stevens and Clayton (1971) analysed belemnites from New Zealand with Bajocian to
685 Tithonian ages at a palaeolatitude of around 80° S (van Hinsbergen et al., 2015). Their
686 specimens recorded $\delta^{18}\text{O}_{\text{shell}}$ values up to 0.43 ‰, but also considerably lower values around
687 -4 ‰ (with outliers as low as -8.5 ‰), some of which might be diagenetically altered.
688 Podlaha et al. (1998) also analysed $\delta^{18}\text{O}_{\text{shell}}$ values of Late Jurassic belemnites of New
689 Zealand and recorded a large variability in the results (-4.40 to 1.86 ‰; with one outlier at
690 -10.99 ‰). Similarly, Gröcke et al. (2003) analysed Late Jurassic belemnites from New
691 Zealand, noted a high variability in their oxygen ratios, and connected those to changes in the
692 $\delta^{18}\text{O}_{\text{sea}}$ values (e.g., via the formation of ice sheets or snow) instead of strongly fluctuating
693 water temperatures. Ullmann et al. (2013, 2016) reconstructed water temperatures based on a
694 large number of stable isotope analyses including Late Jurassic belemnites from New
695 Zealand. Their specimens recorded quite variable $\delta^{18}\text{O}_{\text{shell}}$ values ranging between -4.1 to 0.8
696 ‰ for the Oxfordian, -3.0 to 0.5 ‰ for the Kimmeridgian, and -1.3 to 0.8 ‰ for the Early
697 Tithonian. The highest values (up to 1.6 ‰) were reached in the Late Tithonian (Ullmann et
698 al., 2016). Translating these values into absolute water temperatures might be difficult due to
699 uncertainties regarding $\delta^{18}\text{O}_{\text{sea}}$ values at very high latitudes.

700 Price and Sellwood (1997) analysed 26 belemnite rostra and three inoceramid bivalves
701 with a Late Jurassic age from sites of the Deep Sea Drilling Project on the Malvinas
702 (Falkland) Plateau. The authors mentioned a palaeolatitude of 55 - 60° S for the study area in
703 the Late Jurassic, but more recent reconstructions point to a slightly more northern location
704 (53 - 40° S; van Hinsbergen et al., 2015). The studied taxa recorded surprisingly negative
705 $\delta^{18}\text{O}_{\text{shell}}$ values corresponding to very warm temperatures. While Price and Sellwood (1997)
706 argued that the inoceramids were poorly preserved ($\delta^{18}\text{O}_{\text{shell}}$ values between -2.8 and -4.2
707 ‰), they considered most of the belemnites to have a pristine composition. The authors

708 explain the relatively high reconstructed water temperatures (averages for the two study areas
709 of 17.2 and 17.9 °C) by freshwater influx in the semi-enclosed basin. Price and Gröcke (2002)
710 later analysed more Late Jurassic belemnites of the same study area with $\delta^{18}\text{O}_{\text{shell}}$ values
711 ranging between -2.22 and -0.04 ‰ (translating into water temperatures of 12.1 to 21.2 °C).
712 Jenkyns et al. (2012) published TEX_{86} sea-surface temperature reconstructions ranging
713 between 26 to 30 °C for the Malvinas (Falkland) Plateau for the Middle to Late Jurassic. In
714 order to explain these much warmer temperatures, the authors proposed that the analysed
715 belemnites from the same locality lived in colder waters below the thermocline. Most
716 recently, Vickers et al. (2019) used clumped isotope analyses on Late Jurassic to Early
717 Cretaceous belemnites of the Malvinas (Falkland) Plateau and reconstructed warm
718 temperatures between 21 to 28 °C (average: 25 °C). In combination with $\delta^{18}\text{O}_{\text{shell}}$ values of the
719 belemnite rostra, the authors reconstructed surprisingly high $\delta^{18}\text{O}_{\text{sea}}$ values of around +1 ‰.
720 They explained this surprisingly high value with increased evaporation in a semi-enclosed
721 basin.

722 In summary, previous stable isotope analyses of Jurassic fossils from high-latitude
723 locations in the southern hemisphere show relatively scattered and occasionally surprisingly
724 negative $\delta^{18}\text{O}_{\text{shell}}$ values (conventionally indicating very warm water temperatures). Similar to
725 interpretations for the Neuquén Basin, most previous authors have explained this with factors
726 affecting the $\delta^{18}\text{O}_{\text{sea}}$ values (such as freshwater influence). In this regard, the present South
727 American data matches the previous records of other restricted basins very well. At the same
728 time, some previous authors discarded fossils with particularly negative $\delta^{18}\text{O}_{\text{shell}}$ values as
729 poorly preserved, instead of considering other alternative explanations such as freshwater
730 influence or lowered $\delta^{18}\text{O}_{\text{sea}}$ values of polar waters. The validity of very high temperatures
731 reconstructed via the TEX_{86} -palaeothermometer has been questioned by previous authors
732 (compare Vickers et al., 2019). Similarly, the concept of very warm temperatures
733 reconstructed by clumped isotope analyses faces challenges. A $\delta^{18}\text{O}_{\text{sea}}$ value of +1 ‰ at high
734 latitudes during the Late Jurassic should be indeed only local/regional in extent (such as in a
735 restricted basin as proposed by Vickers et al., 2019). Other Jurassic temperature
736 reconstructions for the southern hemisphere exist for the Tethys Ocean (i.e. in India and
737 Madagascar; Fürsich et al., 2005; Alberti et al., 2012a, b, 2019a). These records reflect plate
738 tectonic movements during the rifting between western and eastern Gondwana and do not
739 contribute to the discussion in the present study.

740

741 **Conclusions**

742

743 105 well-preserved belemnites, bivalves, and brachiopods from two main study areas within
744 the Neuquén Basin were analysed for their stable isotope ($\delta^{13}\text{C}$, $\delta^{18}\text{O}$) and elemental (Mg/Ca,
745 Sr/Ca) composition. The combination of the different geochemical proxies allowed the
746 disentanglement of different environmental parameters influencing the study area. Very
747 negative $\delta^{18}\text{O}_{\text{shell}}$ values of oysters in the northern/central part of the basin likely reflect a
748 variable freshwater influence (meso- to brachyhaline conditions) in this region during the
749 Bathonian to Early Oxfordian and Tithonian. Mg/Ca and $\delta^{18}\text{O}_{\text{shell}}$ data from the remaining
750 localities point to rather stable temperature conditions through the studied time intervals.
751 After considering these limitations, it seems likely that water temperatures in the Neuquén
752 Basin stayed between 20 and 25 °C for most of the studied Jurassic time intervals, possibly
753 interrupted by short colder spells in the Late Pliensbachian, Bajocian, and Late Tithonian.
754 High-resolution $\delta^{18}\text{O}_{\text{shell}}$ analysis of an oyster from the Lower Oxfordian points to a
755 seasonality of around 11 °C, if the $\delta^{18}\text{O}_{\text{shell}}$ fluctuations are explained only by temperature.

756

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758

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762

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1153

1154 **Figure captions**

1155

1156 **Fig. 1.** Palaeogeographic reconstructions for the Neuquén Basin during the Jurassic (modified
1157 after Howell et al., 2005). It is still debated whether the volcanic arc separating the basin from
1158 the open ocean consisted of a chain of individual islands (A; Howell et al., 2005) or
1159 constituted a continuous landmass pierced by only one seaway (B; Vicente, 2005). The study
1160 areas are around Zapala (southern sections) and Chos Malal (northern sections).

1161

1162 **Fig. 2.** Schematic map of the study area in the Neuquén Basin (shaded in grey) in
1163 southwestern South America showing the location of the studied sections near Chos Malal in
1164 the north and Zapala in the south.

1165

1166 **Fig. 3.** General lithostratigraphic framework and major facies types for the Jurassic and
1167 Lower Cretaceous of the Neuquén Basin (modified after Howell et al., 2005).

1168

1169 **Fig. 4.** $\delta^{18}\text{O}$ versus $\delta^{13}\text{C}$ values of fossils and sediment samples of the northern sections near
1170 Chos Malal and the southern sections near Zapala.

1171

1172 **Fig. 5.** Results of stable isotope ($\delta^{18}\text{O}$, $\delta^{13}\text{C}$) and element (Mg/Ca, Sr/Ca) analyses of well-
1173 preserved fossils of the northern sections near Chos Malal. Temperatures for $\delta^{18}\text{O}_{\text{shell}}$ values
1174 were reconstructed with the equation of Anderson and Arthur (1983) and a $\delta^{18}\text{O}_{\text{sea}}$ value of -1
1175 ‰ for an ice-free Jurassic world as suggested by Shackleton and Kennett (1975).
1176 Temperatures for Mg/Ca ratios were calculated with the equations of Mouchi et al. (2013) for
1177 oysters and Nunn and Price (2010) for belemnites. Main facies types are based on Howell et
1178 al. (2005) and the age model is based on Ogg et al. (2016).

1179

1180 **Fig. 6.** Results of stable isotope ($\delta^{18}\text{O}$, $\delta^{13}\text{C}$) and element (Mg/Ca, Sr/Ca) analyses of well-
1181 preserved fossils of the southern sections near Zapala. Temperatures for $\delta^{18}\text{O}_{\text{shell}}$ values were
1182 reconstructed with the equation of Anderson and Arthur (1983) and a $\delta^{18}\text{O}_{\text{sea}}$ value of -1 ‰
1183 for an ice-free Jurassic world as suggested by Shackleton and Kennett (1975). Temperatures
1184 for Mg/Ca ratios were calculated with the equations of Mouchi et al. (2013) for oysters and
1185 Nunn and Price (2010) for belemnites. Main facies types are based on Howell et al. (2005)
1186 and the age model is based on Ogg et al. (2016).

1187

1188 **Fig. 7. A, B.** Results of high-resolution stable isotope ($\delta^{18}\text{O}$, $\delta^{13}\text{C}$) analysis of a specimen of
1189 *Gryphaea* sp. (MOZ-PI 11847/13) from the Lower Oxfordian of the Vega de la Veranada near
1190 Chos Malal. Temperatures were calculated with the equation of Anderson and Arthur (1983)
1191 and a $\delta^{18}\text{O}_{\text{sea}}$ value of -1 ‰ (Shackleton and Kennett, 1975) and alternatively -6.5 ‰. **C.**
1192 $\delta^{18}\text{O}$ versus $\delta^{13}\text{C}$ values of the oyster used for the high-resolution stable isotope analysis
1193 shows a weak positive correlation.

1194

1195 **Fig. 8.** Sr/Ca_{sea} ratios reconstructed from fossils of the Neuquén Basin compared to data of
1196 Ullmann et al. (2013, 2016) and the $^{87}\text{Sr}/^{86}\text{Sr}$ curve of Wierzbowski et al. (2017).

1197

1198 **Fig. 9.** Possible processes affecting the $\delta^{18}\text{O}_{\text{sea}}$ and $\delta^{18}\text{O}_{\text{shell}}$ values in marginal seas. Influx of
1199 marine waters from the open ocean can change the $\delta^{18}\text{O}_{\text{sea}}$ values positively or negatively
1200 depending on their origin. Diagenetic alteration generally leads to a decrease in $\delta^{18}\text{O}_{\text{shell}}$
1201 values. Weathering of volcanoclastics on the sea floor, sea-ice formation, and freshwater
1202 influx lower $\delta^{18}\text{O}_{\text{sea}}$ values. In contrast, evaporation leads to an increase in $\delta^{18}\text{O}_{\text{sea}}$ values.

1203

1204 **Fig. 10.** Compilation of available temperature reconstructions for the Jurassic and Early
1205 Cretaceous of South America based on Mg/Ca ratios and $\delta^{18}\text{O}_{\text{shell}}$ values of bivalves,

1206 belemnites, and brachiopods of Argentina and Chile (data combined from the present study
1207 and Bowen, 1963; Gómez-Dacal et al., 2018; Alberti et al., 2019b). Temperatures for Mg/Ca
1208 ratios were calculated with the equations of Mouchi et al. (2013) for oysters and brachiopods
1209 and Nunn and Price (2010) for belemnites. Temperatures for $\delta^{18}\text{O}_{\text{shell}}$ values were
1210 reconstructed with the equation of Anderson and Arthur (1983) and a $\delta^{18}\text{O}_{\text{sea}}$ value of -1‰
1211 for an ice-free Jurassic world as suggested by Shackleton and Kennett (1975). Temperatures
1212 calculated for bivalves of the northern sections were tentatively corrected by using more
1213 negative $\delta^{18}\text{O}_{\text{sea}}$ values to acknowledge a likely freshwater influence in this region. The trend
1214 lines for benthic taxa and belemnites are based on average values and only serve as
1215 orientation and broad indicators for potential long-term trends as some time intervals are not
1216 covered by data. The age model is based on Ogg et al. (2016).