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1 **Oxygen isotope disequilibrium in the juvenile portion of oyster**
2 **shells biases seawater temperature reconstructions**

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23

24

25 **Abstract**

26

27 For decades, bivalve shells have constituted one of the most common supports for
28 paleoclimatic archives based on stable isotope approaches. In this work, we conducted
29 chemical marking and recapture techniques to study the fluctuation of $\delta^{18}\text{O}$ values of oyster
30 shells of the species *Magallana gigas* reared in natural environment in Normandy (France) for
31 two years. The results were compared to the continuous monitoring of temperature and
32 salinity and monthly records of seawater $\delta^{18}\text{O}$. Isotopic measurements were performed on the
33 hinge area that regroups the whole life of the oysters. Here we demonstrate that oysters
34 mineralized their shells with no significant growth breaks during the two-years experiment,
35 even at temperatures below 6 °C. The results confirm that adult oysters (i.e. > 1 yr)
36 mineralized their shells at equilibrium. However, juvenile specimens exhibit a strong isotopic
37 disequilibrium, with a maximum shift of the $\delta^{18}\text{O}$ values of 3 ‰ in winter, likely due to
38 kinetic isotope effects. This corresponds to a reconstructed temperature up to 13 °C warmer
39 than expected. This work indicates that although these oyster shells can be used as an accurate
40 archive of (paleo)environmental conditions, the shell portion mineralized during the juvenile
41 stage (i.e. < 1 yr) should be avoided for paleotemperature reconstructions. Given the wide use
42 of bivalve shells as environmental archives, similar studies on others species are required.

43

44 **Keywords:** stable isotopes; paleoclimatology; sclerogeochemistry; sclerochronology; kinetic
45 isotope effect

46 1. Introduction

47

48 Since the precursor works of Urey (1947) and Epstein et al. (1951), measurement of
49 the oxygen stable isotope composition of carbonates, namely $\delta^{18}\text{O}$, has been the most
50 common approach used to reconstruct past seawater temperatures. These works have shown
51 that in calcium carbonate minerals, the $\delta^{18}\text{O}$ value is a function of both the temperature and
52 the $\delta^{18}\text{O}$ composition of seawater ($\delta^{18}\text{O}_w$). In shallow marine environments, this method has
53 been broadly applied to mollusks, as they are potentially long-living organisms and the high-
54 resolution measurement of the $\delta^{18}\text{O}$ value of their shells ($\delta^{18}\text{O}_{\text{shell}}$) allows for the
55 reconstruction of present and past seasonal gradients of seawater temperatures (e.g. Jones and
56 Quitmyer, 1996; Purton and Brasier, 1997; Kirby et al., 1998; Surge et al. 2001, 2003;
57 Kobashi et al., 2001; Latal et al., 2004; Schöne et al., 2004; Lartaud et al., 2010a; Harzhauser
58 et al., 2011; Wanamaker et al., 2012; Mette et al., 2016; Reynolds et al., 2017; Briard et al.,
59 2020).

60 One of the prerequisites for using $\delta^{18}\text{O}$ values for (paleo)environmental
61 reconstructions is to determine if the organisms mineralize their shell in isotopic equilibrium
62 with seawater. So-called isotopic disequilibrium has been identified for taxa, such as the
63 coccolithophores, foraminifers or corals (McConnaughey et al., 1997; Spero et al., 1997;
64 Adkins et al., 2003; Hermoso et al., 2016). Isotopic disequilibria are on the contrary reputed
65 to be nonexistent or negligible for most marine mollusk species (Wefer and Berger, 1991;
66 Chauvaud et al., 2005; Schöne et al., 2005; Peharda et al., 2019), although exceptions have
67 been reported for some species, such as deep sea oysters of the genus *Pycnodonte* (Wisshak
68 et al., 2009) or the giant scallop, *Pecten maximus* (Owen et al., 2002). Kinetic isotope effects
69 induced by anomalously low or high growth rates have been proposed by these authors, in
70 addition to the combined effects of environmentally ‘stressful’ conditions (e.g., low

71 temperature, low salinity), as causes of disruptions in isotopic equilibrium (Owen et al., 2008;
72 Lartaud et al., 2010c). Finally, a recent study demonstrates that most of biogenic carbonates
73 do not unequivocally precipitate at isotopic equilibrium and suggests revising the classic
74 thermodynamic model (Daëron et al., 2019).

75 In depth work is thus required to characterize the conditions under which mollusks
76 form their shells at isotopic equilibrium. Among the mollusk shells used as environmental
77 archives, shallow-water oysters are considered as important model species, as many studies
78 have shown that their oxygen stable isotope signature can provide reliable information about
79 their living conditions using oxygen stable isotopes geochemistry (Wefer and Berger, 1991;
80 Richardson et al., 1993; Kirby et al., 1998; Surge et al. 2001, 2003; Lécuyer et al., 2004;
81 Lartaud et al., 2010a, 2010b; Ullmann et al. 2010; Tynan et al. 2014), or magnesium-calcium
82 ratios (Surge and Lohmann, 2008; Mouchi et al., 2013; Tynan et al., 2017). Oysters are
83 ubiquitous and abundant organisms found in shallow marine and brackish deposits since the
84 Jurassic and mineralize their shells with calcite materials, making them resistant to diagenesis.
85 Oyster shells are thus commonly used to reconstruct the mean annual and seasonal gradient of
86 paleotemperatures of near shore environments (Kirby et al., 1998; Kirby, 2000, 2001; Brigaud
87 et al., 2008; Lartaud et al., 2010a; Harzhauser et al., 2011; Huyghe et al., 2012; Briard et al.,
88 2020).

89 To use shell material as a (paleo)environmental parameter archive, a precise growth
90 chronology allowing to properly refer each carbonate micro-sampling to a calendar date must
91 be determined. This type of approach is widely used in bivalve shells such as *Arctica*
92 *islandica* or *Pecten maximus* that mineralize one increment each year and each day during
93 part of the year respectively (Schöne et al., 2004; Chauvaud et al., 2005; Mette et al., 2016).
94 On the contrary, it was demonstrated that oysters do not precipitate calcitic increments at
95 regular time intervals throughout their life (i.e., several growth anomalies were reported

96 during the juvenile period while growth is strongly tidal related after; Huyghe et al., 2019).
97 Thus, to get around this limit, we used mark and recapture experiments based on regular
98 chemical staining of shells, combined with sclerochronological techniques (Lartaud et al.,
99 2010d; Nedoncelle et al., 2013). The resulting shell growth model revealed under
100 cathodoluminescence (CL) observations, demonstrated the validity of using this type of
101 biogenic material (Langlet et al., 2006; Lartaud et al., 2010d). This growth model,
102 significantly revised by Huyghe et al. (2019) provides a suitable framework to test if
103 mineralization occurs in isotopic equilibrium during the entire specimen lifetime. .

104

105

106 **2. Materials and methods**

107

108 *2.1. The Magallana gigas oyster*

109

110 This work focuses on the analysis of oysters of the species *Magallana gigas*, which
111 corresponds to the former *Crassostrea gigas* (Salvi and Mariottini, 2017). These oysters are
112 widely raised commercially in shallow water environments. They tolerate large variations of
113 water salinity, temperature and turbidity. *Magallana gigas* oysters are suspension feeders and
114 sequentially hermaphrodites, reaching sexual maturity at 12 to 18 months in the studied area
115 (Soletchnik et al., 1996). Reproduction occurs during summer on the French Atlantic coast,
116 but in the location of this work, in the English Channel, the temperature generally remains too
117 cold for reproduction (Ropert et al., 2007), which forces shellfish-farmers to import spats
118 from more southern French locations. In the present study, we consider specimens of less than
119 12 months as juveniles (i.e. before summer 2005) and specimens older than 12 months as sub-
120 adults according to the age when sexual maturity starts for these oysters.

121

122 2.2. *Breeding site and breeding conditions*

123

124 Young oysters (< 6 months old) were reared for 2 years in an experimental site of the
125 *Institut Français de Recherche pour l'Exploitation de la Mer* (IFREMER), located on the
126 Normandy coast of the English Channel, at the Baie des Veys (BDV, 49°23.110'N
127 1°6.050'W), following the protocol described in Lartaud et al. (2010d). The BDV is an open
128 bay characterized by a high intertidal setting and semi-diurnal tide regime (Huyghe et al.,
129 2019). Young (< 6 months) and small-sized (< 2 cm) specimens of *M. gigas* were collected
130 from wild broodstock at the Arcachon Basin (Gironde, France), at the end of January 2005
131 and were then transferred to the BDV for growth experiments. The shells were cultivated on
132 oyster tables from the January 28, 2005 to November 28, 2006. Oysters were reared on tables
133 50 cm above the sediment. Maximum water depth was 6m above the tables and they were
134 emerged during maximum 3 hours per day during periods of low waters spring tides (Huyghe
135 et al., 2019). Hourly measurements of seawater temperature and salinity were directly
136 conducted at the sampled oyster for this study using a multi-parameter probe (YSI data
137 logger, IFREMER) from January 2005 to November 2006 (Huyghe et al., 2019; Fig. 1). The
138 water temperature on the oyster tables ranged from 4.8 to 20 °C and fluctuated seasonally
139 with mean summer (July to September) and winter (January to March) temperatures of
140 18.7±0.6 and 6.7±1.1 °C respectively (Huyghe et al., 2019; Fig. 1). Salinity remained quite
141 stable over the year (33.3±0.7) and displayed only episodic freshwater inputs, which reduced
142 values to 28.8, following heavy rainfalls (Fig. 1).

143 To assign a growth calendar and link the isotope records of biogenic calcite material
144 with the fluctuation of the environmental parameters, we used a mark and recapture technique
145 combined with the sclerochronological analysis of shells (Lartaud et al., 2010d; Huyghe et al.,

146 2019). Oyster shells were stained at nearly regular intervals (i.e., 15 times during the whole
147 breeding phase) on site with Mn^{2+} following the protocol of Langlet et al. (2006). For each
148 staining, oysters were immersed for 4 hours during low tide in a tank filled with seawater in
149 which 90 mg.l^{-1} of manganese chloride tetrahydrate ($MnCl_2 \cdot 4H_2O$) was added. Oysters were
150 sampled in November 2006 and shells were then sectioned and mounted on thin sections for
151 CL observations. Rapid incorporation of Mn^{2+} into the shell calcite appeared as highly
152 luminescent micro-growth bands under CL (Fig. 2; Langlet et al., 2006; Barbin et al., 2008).
153 The identification of the successive Mn^{2+} -markings and the use of tidal CL increments in shell
154 sections allowed for the determination of growth rates over the corresponding time intervals
155 and the identification of a high-resolution calendar growth profile (Fig. 2; Huyghe et al.,
156 2019).

157

158 *2.3. Shell preparation and isotope analyses*

159

160 Immediately upon collection, the oysters were carefully opened and the flesh was
161 scrapped and removed from the inner surface of the shell valves. Upon return to the
162 laboratory, the shells were placed in a 6 % solution of hydrogen peroxide (H_2O_2) for 6 hours
163 to remove any epibionta from the outer shell surfaces, washed in 0.15 N nitric acid for 20
164 minutes to dissolve any carbonate based superficial contamination and rinsed in
165 demineralized water. Observations and samplings were made on the hinge area of the oysters
166 that compiles a complete ontogenetic record of both oyster hinge growth and environmental
167 conditions experienced throughout their lives (Lartaud et al., 2010d). The dry left valve of the
168 shell was cut longitudinally along the growth axis at the umbo region, and thin sections were
169 manufactured to expose the preserved internal structures in order to perform CL observation
170 of the foliated low-magnesium calcite of the hinge region. Mn^{2+} markings were revealed

171 under CL microscopy observations (Fig. 2) with a cold cathode (Cathodyne-OPEA, 15-20 kV
172 and 200-300 $\mu\text{A}\cdot\text{mm}^{-2}$ under a pressure of 0.05 Torr).

173 Shell calcium carbonate samples for $\delta^{18}\text{O}_{\text{shell}}$ analyses were drilled to a depth of 100
174 μm along each thin section growth profile in the hinge region. We used a 0.3 mm drill bit and
175 a computer assisted micromill. Samplings were performed at low and constant speed. The
176 corresponding dates for each drilled sample were assigned using the CL growth profile
177 previously described (Fig. 2). The collected carbonate powders were acidified in 100 %
178 H_3PO_4 at 50 °C under vacuum. The CO_2 produced was collected and analyzed using a VG
179 Instruments Isoprime mass spectrometer. Isotopic data were reported in conventional delta (δ)
180 notation relative to the Vienna Pee Dee Belemnite (VPDB). The standard used for the
181 analyses was an internal standard calibrated on the NBS-19. Standard deviation for $\delta^{18}\text{O}$
182 values was $\pm 0.1 \text{‰}$.

183

184 2.4. $\delta^{18}\text{O}$ seawater analyses

185

186 Sub-monthly analyses of seawater oxygen isotopic composition ($\delta^{18}\text{O}_w$) were also
187 performed to determine their seasonal variation. We used the method described in Pierre et al.
188 (1994) for water sampling and analyses. The water samples were collected during high tides,
189 above the oyster tables, in 100 ml glass bottles. CO_2 -water equilibration method of Epstein
190 and Mayeda (1953) was used as the analytical procedure for the CO_2 preparation in order to
191 measure the $\delta^{18}\text{O}_w$ values.

192 The isotopic compositions were determined using a VG Micromass 602 mass
193 spectrometer. The analytical reproducibility was within the range $1\sigma = 0.1\text{‰}$ for $\delta^{18}\text{O}$ values.
194 The δ values correspond to the per mil deviation of the sample relative to the SMOW
195 reference and PDB reference respectively.

196

197

198 **3. Results**

199

200 *3.1 Seawater isotopic composition*

201

202 Measurements of the $\delta^{18}\text{O}_w$ values are reported on Fig. 1. This parameter exhibited
203 little seasonal variation with a mean value of $-0.1 \pm 0.1 \text{ ‰}$. The minimum value was observed
204 in March 2005 (-0.3 ‰), whereas the maximum values occurred in August 2005 and 2006
205 ($+0.1 \text{ ‰}$). $\delta^{18}\text{O}_w$ values fluctuations are not correlated with temperature ($r = 0.50$; $p < 0.05$),
206 and reflects salinity values ($r = 0.68$; $p < 0.05$) that also remained constant on the breeding
207 site.

208

209 *3.2. Comparison of the shell oxygen isotope ratios with the predicted values at* 210 *isotopic equilibrium*

211

212 Figure 3 reports the time distribution of the $\delta^{18}\text{O}_{\text{shell}}$ values for four oyster shells. They
213 exhibited a large seasonal range but a small inter-shell variability. Except for the high values
214 in February 2005 (-0.2 to -0.5 ‰), values ranged between $+1.5$ and $+2.2 \text{ ‰}$ in winter and -0.5
215 ‰ and -1.2 ‰ in summer.

216

217 Determining whether shells precipitate in oxygen isotope equilibrium with seawater
218 requires the estimation of the $\delta^{18}\text{O}_{\text{shell}}$ value expected at equilibrium into the shell carbonate
219 lattice from the temperature and $\delta^{18}\text{O}_w$ values measured in the breeding environment. In the
219 following, we consider isotopic equilibrium in the sense of Kim and O'Neil (1997), which is
220 an apparent equilibrium achieved by most of biogenic carbonates as demonstrated by Daëron
221 et al. (2019). According to temperatures monitored at an subdaily time step (Fig. 2) and $\delta^{18}\text{O}_w$

222 values measured in the oyster area, $\delta^{18}\text{O}_c$ values expected at equilibrium (i.e., $\delta^{18}\text{O}$ values
223 predicted 1 in Fig. 3) was estimated using the equation of Kim and O'Neil (1997):

224

$$225 \quad T = 18030 / (1000 \ln \alpha + 32.17) - 273.15 \quad (\text{equation 1})$$

226

$$227 \quad \text{with } \alpha = (1000 + \delta^{18}\text{O}_{\text{shell}}) * (1000 + \delta^{18}\text{O}_w) \quad (\text{equation 2})$$

228

229 We converted the $\delta^{18}\text{O}_{\text{shell}}$ expressed in SMOW to PDB value according to the
230 equation of Coplen et al. (1983).

231

$$232 \quad \delta^{18}\text{O}_c (\text{SMOW}) = (1.03091) * (\delta^{18}\text{O}_{\text{shell}} (\text{PDB}) - 0.25) + 30.91 \quad (\text{equation 3})$$

233

234 The $\delta^{18}\text{O}_w$ values were monitored in the breeding site by discrete, sub-monthly water
235 sampling, which excludes the interpretation of possible high-resolution fluctuations. But,
236 using Lartaud et al. (2010a) relationship between $\delta^{18}\text{O}_w$ values and salinity for various oyster
237 sites from the English Channel and the Atlantic coast of France, including the BDV location,
238 and the subdaily monitoring of salinity in the oyster breeding area, high-resolution $\delta^{18}\text{O}_w$
239 values were calculated as follows:

240

$$241 \quad \delta^{18}\text{O}_w (\text{‰}) = 0.22 S (\text{‰}) - 7.30 \quad (\text{equation 4})$$

242

243 where $\delta^{18}\text{O}_w$ is the $\delta^{18}\text{O}$ value of seawater in SMOW and S the salinity. This approach was
244 used to obtain a second estimation of $\delta^{18}\text{O}$ value expected at equilibrium (i.e., predicted 2 in
245 Fig. 3).

246 Both models of predicted $\delta^{18}\text{O}$ values were in good agreement ($r = 0.99$; $p < 0.05$)
247 (Fig. 3), showing that the use of an estimation of $\delta^{18}\text{O}_w$ value through salinity measurements
248 is accurate enough for this type of approach in the environmental settings for which the study
249 was conducted.

250 We observed on Fig. 3 that during the first six months of the experiment, $\delta^{18}\text{O}_{\text{shell}}$
251 values exhibit a significant shift compared to the predicted values at isotopic equilibrium.
252 First, during January and the beginning of February, $\delta^{18}\text{O}_{\text{shell}}$ values are 0.3 to 1‰ lower than
253 the predicted $\delta^{18}\text{O}$. During the second half of February, the isotopic shift increases with shell
254 values more negative by 1.7 to 3‰. Then, from March to June, $\delta^{18}\text{O}_{\text{shell}}$ values remain
255 constant for a given shell, and the shift with the predicted values decreases continuously.
256 Once the organisms reached 1 year old (i.e., during summer 2005), values measured in shells
257 were close to values predicted at isotopic equilibrium.

258

259

260 **4. Discussion**

261

262 *4.1. A juvenile isotopic disequilibrium*

263

264 The results observed on Fig. 3 suggest that mineralization occurs out of equilibrium
265 for oxygen isotopes during the younger part of the life of oysters (i.e., < 1 year old). To
266 quantify this disequilibrium compared to theoretical values for calcite and biocalcite, we
267 plotted on Fig. 4 the coefficient of fractionation between water and calcite $\alpha_{c/w}$ as a function
268 of the calculated temperature of mineralization. Two distinct equilibriums were considered:
269 (i) the empirical relationship of Kim and O'Neil (1997) for synthetic calcites, and (ii) that of
270 Watkins et al. (2014) and Daëron et al. (2019) for natural slow growing calcites. These

271 relationships yield the same dependency on temperature but the Kim and O'Neil (1997)
272 model has a constant offset of -1.5 ‰. The shell portion mineralized during winter and spring
273 2005 (i.e., during the most juvenile stage of the oysters in the data set), differs greatly from
274 the equilibrium of both the synthetic and slow growing calcites. Various parameters have
275 been proposed to generate isotopic disequilibria in calcites, such as pH of seawater, solution
276 saturation and crystallization rate (Watkins et al., 2014; Devriendt et al., 2017). As these
277 environmental parameters did not differ significantly between winter and spring 2005 (i.e.,
278 juvenile oysters) and winter and spring 2006 (i.e., adult oysters), it is unlikely that pH of the
279 seawater or solution saturation could have changed enough to impact the isotopic equilibrium
280 to such a degree. A recent study, which investigated growth patterns of oyster shells from the
281 same spat as the one used in this experiment revealed that during the juvenile part of the shell,
282 growth is characterized by high growth rates (up to 180 $\mu\text{m}/\text{day}$ in the hinge area), and severe
283 anomalies in the rhythm of deposition of calcite material (Huyghe et al., 2019). Lower $\delta^{18}\text{O}$
284 values in biogenic material relative to the expected isotopic equilibrium have been suggested
285 to result from kinetic fractionation due to rapid mineralization and the influence of rebalance
286 in the internal fluid pH on the dissolved inorganic carbon species (McConnaughey et al.,
287 1997; Adkins et al., 2003; Dietzel et al., 2009; Uchikawa and Zeebe, 2012). For example,
288 Rollion-Bard et al. (2008) showed that early precipitated calcite is depleted by 3 ‰ compared
289 to secondary calcite in foraminifera tests, due to elevated pH in the calcification fluid. Owen
290 et al. (2002) also showed that for *P. maximus* shells, the $\delta^{18}\text{O}_{\text{shell}}$ value is more depleted
291 during fast growth rate intervals and these deviations have been interpreted as resulting from
292 kinetic isotope effects. However, in their work, Owen et al. (2002) described a maximum
293 negative shift in the $\delta^{18}\text{O}_{\text{shell}}$ value of 1 ‰ whereas here the juvenile oyster shells show a
294 maximum negative shift of 3 ‰ (Fig. 3), closer to the isotopic disequilibrium described for
295 corals and foraminifera (Devriendt et al., 2017). Reaching equilibrium between dissolved

296 carbonate species and water via hydration and hydroxylation reactions requires a minimum
297 residence time in the calcifying fluid estimated at 1h for corals (Rollion-Bard et al., 2003).
298 Staining experiments revealed that calcification occurs in less than 30 min for oysters
299 (Lartaud et al., 2010d). Assuming high growth rates (up to 180 μm / day) in a short period of
300 time during the juvenile stage of oysters (Huyghe et al., 2019), conditions for such strong
301 isotopic disequilibrium exist.

302 The shift observed between measured and predicted $\delta^{18}\text{O}$ values is not constant as the
303 difference between the $\delta^{18}\text{O}_{\text{shell}}$ values of the three shells and the predicted $\delta^{18}\text{O}$ values at
304 equilibrium decreases dramatically until May-June 2005 ($\sim 0.5\text{‰}$) (Fig. 3), leading to an $\alpha_{c/w}$
305 closer to the Kim and O'Neil (1997) equilibrium (Fig.4). This is in agreement with strong but
306 highly variable growth rates during the juvenile stages (Huyghe et al., 2019), leading to
307 periods where conditions to reach equilibria are closer. These results support the model of
308 Coplen et al. (2007) and Daëron et al. (2019) for which only carbonates precipitating at very
309 slow rates can precipitate at isotopic equilibrium.

310 Contrary to the juvenile phase, the shell portion formed in the adult phase (> 1 year
311 old) appears consistent with the theoretical isotopic equilibrium of Kim and O'Neil (1997),
312 but still differs substantially from the theoretical and measured equilibrium for slow-growing
313 calcites by Watkins et al. (2014) and Daëron et al. (2019), respectively (Fig. 4). This
314 difference implies that the shells calcify too rapidly to achieve DIC-calcite equilibrium. But as
315 the slopes of the equilibrium regression are the same, we conclude that both the equilibrium
316 limit and the kinetic limit of $\alpha_{c/w}$ do not vary significantly with temperature. Although shells
317 do not reach an exact isotopic equilibrium according to Daëron et al. (2019), temperature can
318 be inferred from the Kim and O'Neil (1997) empirical equation.

319

320

4.2. Paleoclimatic implications

After the first year of life, labeled here as the juvenile phase, our results show that oysters mineralize their shells close to the isotopic equilibrium and thus can accurately reflect the seawater temperatures, assuming an independent estimation of the isotopic composition of seawater. This confirms the use of this type of biogenic material as a promising paleoclimate archive, as revealed by the large bibliography on modern and fossil oysters (Kirby et al., 1998; Surge et al., 2001, 2003; Harding et al., 2010; Lartaud et al., 2010a; Harzhauser et al., 2011; Bougeois et al., 2014; Tynan et al., 2014; Huyghe et al., 2015; Briard et al., 2020).

The measured seawater temperatures were plotted versus the difference between $\delta^{18}\text{O}_{\text{shell}}$ values of oyster shells and the $\delta^{18}\text{O}_{\text{w}}$ values estimated through salinity monitoring (equation 4) (Fig. 5). The data for the juvenile phase (February to June 2005) were excluded, as the oysters did not mineralize their shell in isotopic equilibrium during this interval. A negative linear correlation was found between the shell and seawater oxygen isotopes differences ($\delta^{18}\text{O}_{\text{shell}} - \delta^{18}\text{O}_{\text{w}}$) and the seawater temperatures measured by the probes deployed in situ (least mean squares regression, $R^2 = 0.87$, $p < 0.05$, $n=60$):

$$T (\text{°C}) = 15.26(\pm 0.17) - 4.26(\pm 0.22) (\delta^{18}\text{O}_{\text{shell}} - \delta^{18}\text{O}_{\text{w}}) \quad (\text{equation 5})$$

With $\delta^{18}\text{O}_{\text{shell}}$ in PDB and $\delta^{18}\text{O}_{\text{w}}$ in SMOW.

Different types of equations to link the $\delta^{18}\text{O}$ values of calcitic bivalve shells to temperatures exist, with the most currently used are those from Friedman and O'Neil (1977) and Kim and O'Neil, (1997), based on synthetic calcite, and Anderson and Arthur (1983), established from various carbonates including mollusk shells. Figure 6 reports the seawater temperature measured at the BDV over the studied interval compared to the temperatures

346 calculated from the $\delta^{18}\text{O}$ values of the four combined shells according to different equations.
347 Kim and O'Neil (1997) (equation 2) and the one issued from this study (equation 5) were
348 used, as well as the equation 6 of Friedman and O'Neil (1977) modified from Tarutani et al.
349 (1969):

$$350 \quad 1000 \ln \alpha = (2.78 * 10^6) / T^2 (\text{K}) - 2.89 \text{ (equation 6)}$$

$$351 \quad \text{with } \alpha = (\delta^{18}\text{O}_{\text{shell SMOW}} + 1000) / (\delta^{18}\text{O}_{\text{w SMOW}} + 1000) \text{ (equation 7)}$$

352

353 and the equation 8 resulting from Anderson and Arthur (1983):

354

$$355 \quad T (\text{°C}) = 16 + 4.14 (\delta^{18}\text{O}_{\text{c}} - \delta^{18}\text{O}_{\text{w}}) + 0.13 (\delta^{18}\text{O}_{\text{c}} - \delta^{18}\text{O}_{\text{w}})^2 \text{ (equation 8)}$$

356

357 Temperatures calculated from the four equations during early phase of the juvenile
358 portion of shells, (i.e., from February to March 2005) is up to ~ 13 °C warmer than the
359 measured ones. Calculated temperatures differ from the measured temperatures until July
360 2005, due to the isotopic disequilibrium described earlier (Fig. 6). From August 2005, the four
361 equations yield very similar values to measured temperatures, although the Friedman and
362 O'Neil (1977) and Anderson and Arthur (1983) equations exhibit a shift of + 2 °C and +2.5
363 °C in winter 2006 respectively compared to the measured temperatures. This significant
364 positive difference suggests that the Friedman and O'Neil (1977) and Anderson and Arthur
365 (1983) equations are not appropriate enough to reconstruct colder temperatures with oyster
366 shells, at least in temperate climates.

367 These results are of major importance because they show that the choice of T- $\delta^{18}\text{O}$
368 values relationship can alter the reconstruction of the seasonal range of seawater temperature
369 from $\delta^{18}\text{O}$ analyses. Although the equations of Kim and O'Neil (1997) and the one from this
370 study can deviate slightly from measured values, they generally fit better with the observed

371 seasonal variations. As the temperatures estimated by these two equations differ on average
372 by only 0.6 °C during winter and 0.9 °C during summer, we suggest using preferentially the
373 equation of Kim and O'Neil (1997) which is already widespread in the literature.

374 In addition, the reconstructed temperatures based on oxygen isotopes highlight that
375 oyster are able to mineralize their shells during winter in seawater temperatures as cold as 5.7
376 °C. This value is close to the minimum temperature for oyster biomineralization proposed by
377 Ullmann et al. (2010), deduced from stable isotopes analysis, and by Huyghe et al. (2019)
378 from counting growth increment.

379

380

381 **5. Conclusions**

382

383 Oxygen isotope measurements of oyster shells of the species *Magallana gigas* enabled
384 us to identify the parameters controlling the stable isotope composition in their shells. We
385 demonstrate that oysters mineralize their shell at isotopic equilibrium during the adult part of
386 their life (i.e., specimens more than one year old). Oysters shells are thus reliable archives of
387 their living conditions and can be used to accurately reconstruct the seasonal temperature
388 gradient in their environment, even in winter seawater temperatures below 6 °C. The
389 comparison between measured *in situ* temperatures and the temperatures calculated from
390 equations provided by previous studies indicates that the equation of Kim and O'Neil (1997)
391 yields accurate summer and winter temperatures. On the contrary, the equations of Anderson
392 and Arthur (1983) and Friedman and O'Neil (1977) over-estimates winter temperatures by ~ 2
393 °C, which does not reliably constrain the seasonal range of temperature.

394 During the juvenile period, (i.e., during the first year of life), an isotopic fractionation
395 was observed for the $\delta^{18}\text{O}$ values. This shift is maximum during the younger part of the shell

396 observed (corresponding to winter here), and is contemporaneous with anomalous high
397 growth peaks. This deviation can be explained by a kinetic isotope effect due to very high
398 growth rates. We thus recommend avoiding the juvenile interval of oyster shells to reconstruct
399 reliable temperatures. Further works are required to investigate if this kind of isotopic
400 disequilibria associated to the juvenile period can be observed in other species than oysters.

401

402

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404

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410

411 **Contributors**

412 FL, LE, MdR and MRe designed the study. DH, LE, MdR, MRo and FL conducted the field
413 work, and NL and LE carried out the stable isotope analyses. DH and FL wrote the paper. All
414 authors contributed critically to the drafts and gave final approval for publication.

415

416

417 **Conflict of interest:** The authors declare that they have no conflict of interest.

418

419 **Ethical approval:** All applicable international, national, and/or institutional guidelines for the care
420 and use of animals were followed.

421

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424

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612

613 **Figure caption**

614

615 **Figure 1:** Fluctuation of seawater temperature, salinity (from Huyghe et al., 2019) and $\delta^{18}\text{O}$
616 composition of seawater measured above the oyster tables in the Baie des Veys, Normandy,
617 France.

618

619 Figure 2: Illustration of the attribution of an absolute chronological framework to the
620 samplings over the hinge area. A: section of the right part of the hinge area under natural light
621 and illustration of the samplings for stable isotope analyses. The location of the 15 chemical
622 markings are also reported. B: observation of the left section of the hinge under
623 cathodoluminescence allowing for the identification of the Mn^{2+} markings. C:
624 cathodoluminescence profile measured (arbitrary units, AU) along the profile reported in B
625 (white dotted line). High luminescent values correspond to the Mn^{2+} markings. The horizontal
626 axis corresponds to the length measured along the hinge. D: conversion of the length to
627 calendar dates given the dates of the markings and from the counting of the tidal influenced
628 calcitic increments. Horizontal red lines illustrate the fluctuation in the duration of each
629 isotope sample according to the period considered.

630

631 **Figure 3:** Variation through time of the $\delta^{18}\text{O}$ of the four shells analyzed. The $\delta^{18}\text{O}$ values at
632 isotopic equilibrium predicted from Kim and O'Neil (1997) and calculated from the $\delta^{18}\text{O}$ of
633 seawater are shown by the red diamonds ($\delta^{18}\text{O}$ predicted 1). The $\delta^{18}\text{O}$ values calculated from
634 salinity values are shown by the grey line ($\delta^{18}\text{O}$ predicted 2). Note that the vertical (y) axis is
635 inverted.

636

637 **Figure 4:** Correlation between the calculated temperatures from $\delta^{18}\text{O}$ of oysters shells using
638 the equation of Kim and O'Neil (1997) and the fractionation coefficient between calcite and
639 water $\alpha_{c/w}$. Comparison is made with the theoretical isotopic equilibrium of Kim and O'Neil
640 (1997) (dotted line) and the equilibrium of slow growing calcites, calculated by Watkins et al.
641 (2014) and Daëron et al. (2019). This comparison highlights that juvenile oyster samples were
642 mineralized out of equilibrium.

643

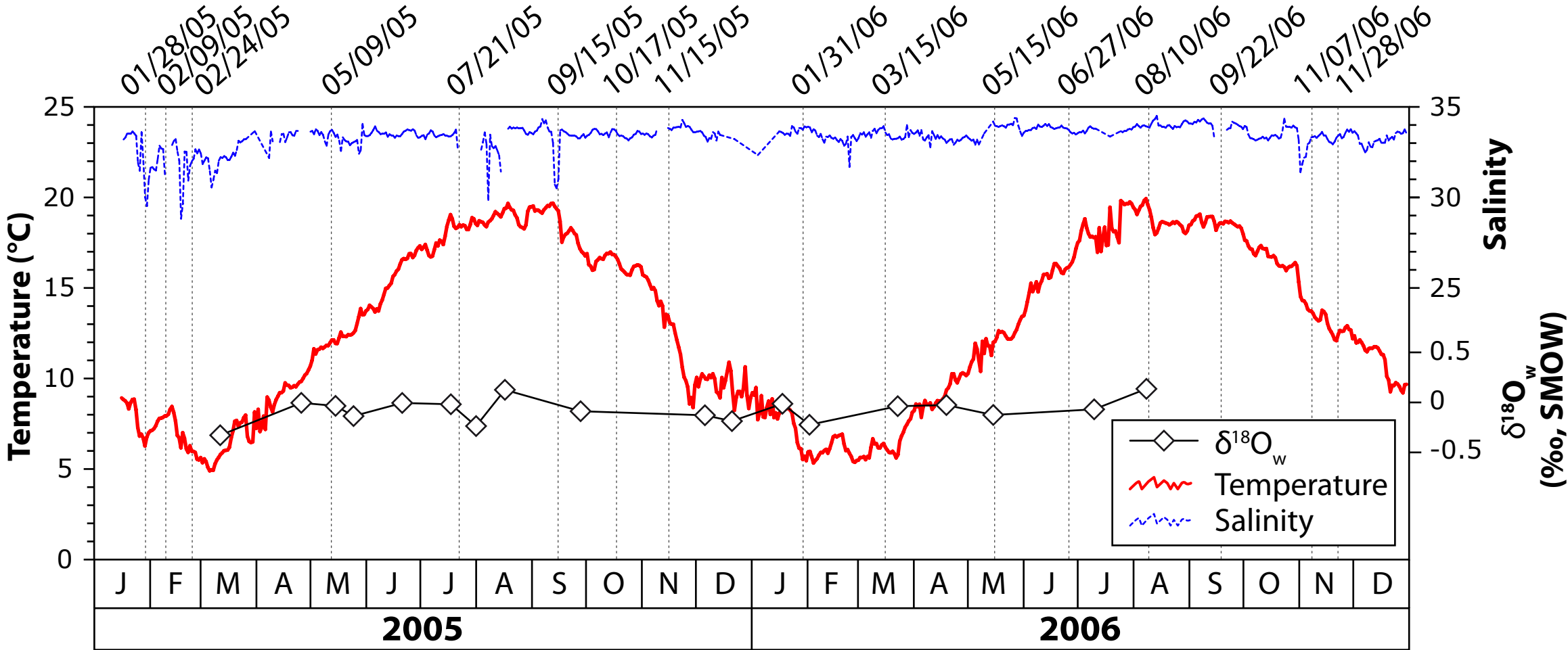
644 **Figure 5:** Temperature equation proposed according to the oxygen isotopes of oyster shells
645 from for the Baie des Veys. Values before July 2005, when shells mineralized out of isotopic
646 equilibrium during the juvenile period, were excluded from the correlation.

647

648 **Figure 6:** Fluctuation over time of the measured seawater temperatures (from Huyghe et al.,
649 2019) and the temperatures calculated from the $\delta^{18}\text{O}$ values of oyster shells using the
650 equations of Friedman and O'Neil (1977), Kim and O'Neil (1997), Anderson and Arthur
651 (1983) and the equation determined from this study.

652

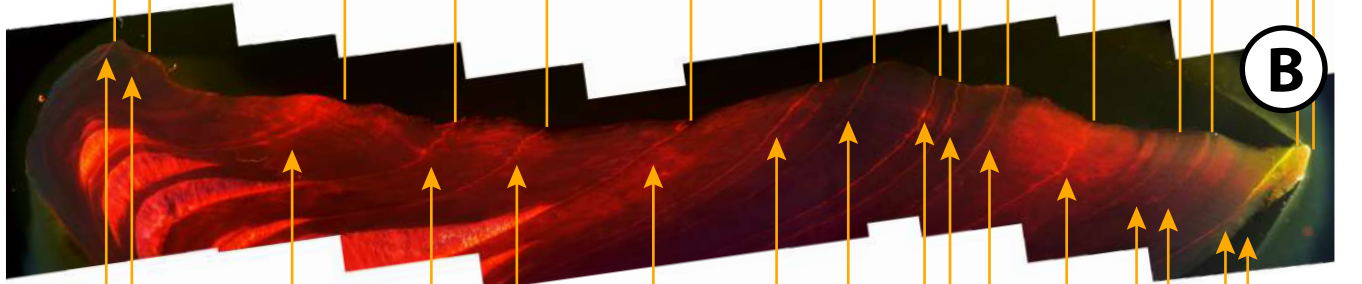
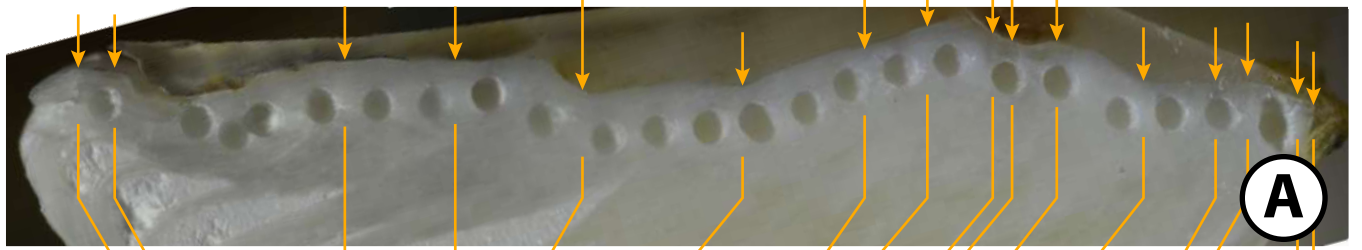
Mn²⁺ markings



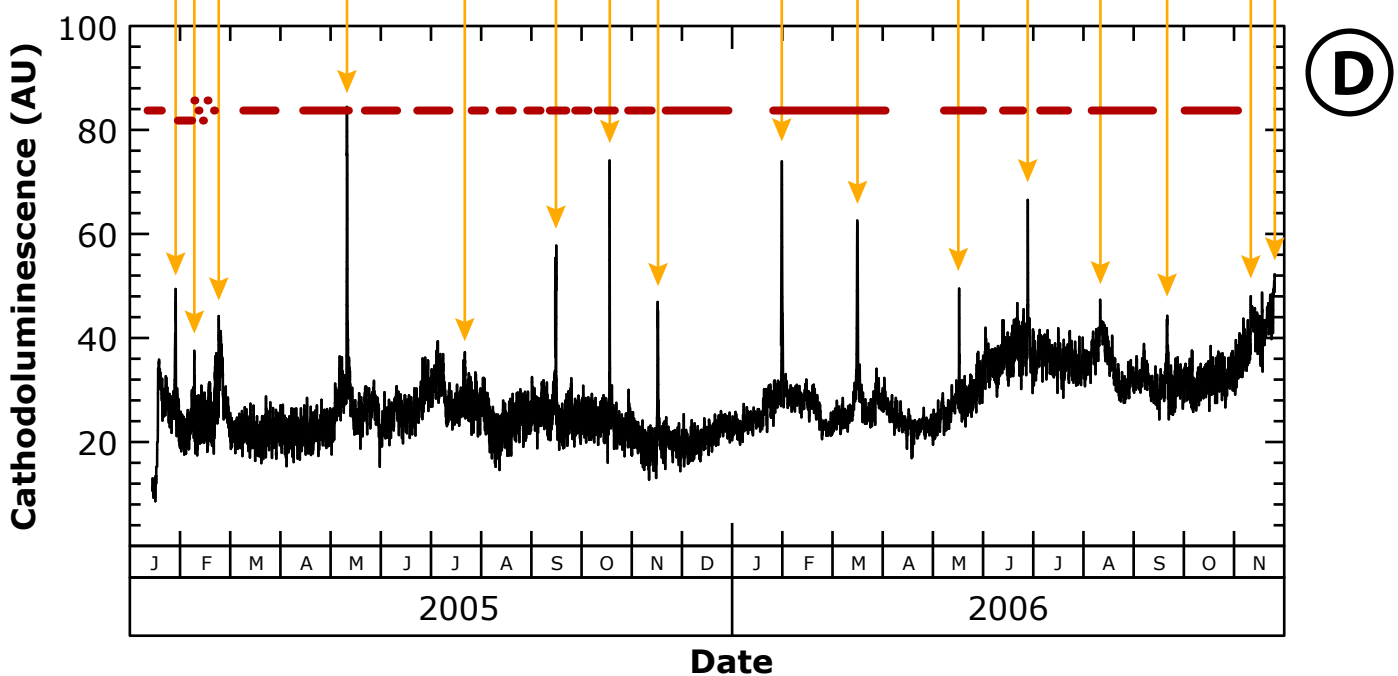
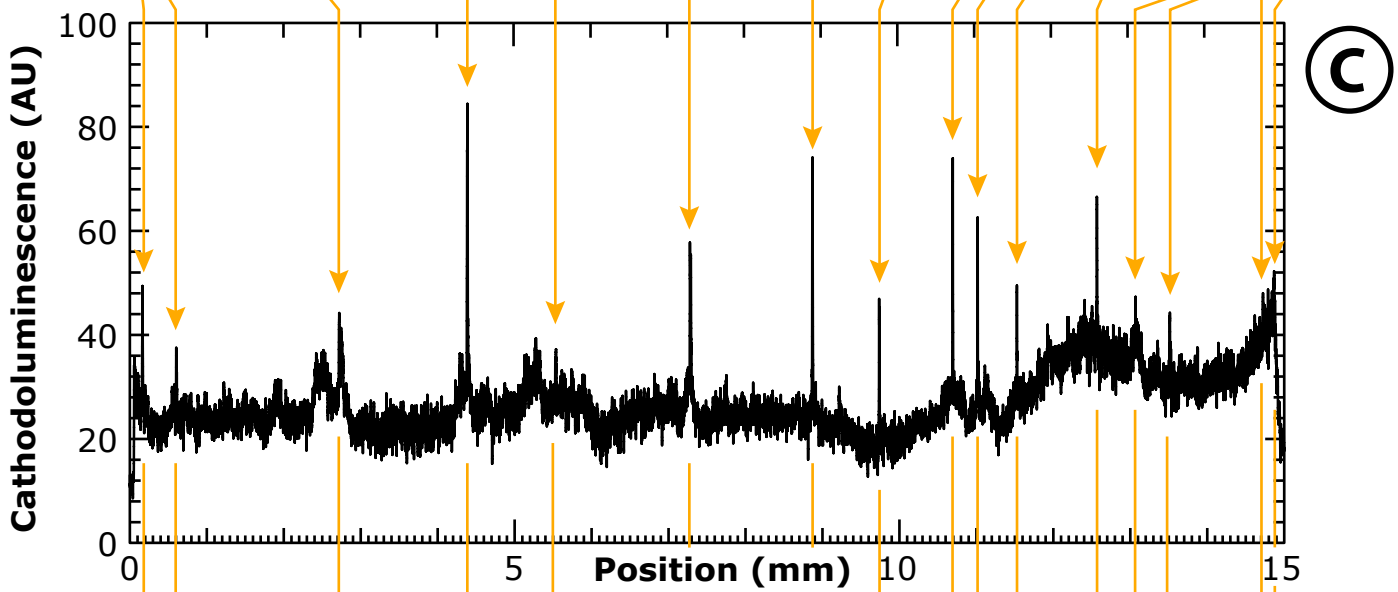
BDV-n6-3

Juvenile

Adult



28/01/05 09/02/05 24/02/05 09/05/05 21/07/05 15/09/05 17/10/05 15/11/05 31/01/06 15/03/06 15/05/06 27/06/06 10/08/06 22/09/06 07/11/06 28/11/06



Mn²⁺ markings

