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**Reconstruction of seasonal temperature variability in the tropical Pacific Ocean from the shell
of the scallop, *Comptopallium radula***

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Running head: Scallop shells as temperature recorders in the Pacific Ocean

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ABSTRACT

We investigated the oxygen isotope composition ($\delta^{18}\text{O}$) of shell striae from juvenile *Comptopallium radula* (Mollusca; Pectinidae) specimens collected live in New Caledonia. Bottom-water temperature and salinity were monitored in-situ throughout the study period. External shell striae form with a 2-day periodicity in this scallop, making it possible to estimate the date of precipitation for each calcite sample collected along a growth transect. The oxygen isotope composition of shell calcite ($\delta^{18}\text{O}_{\text{shell calcite}}$) measured at almost weekly resolution on calcite accreted between August 2002 and July 2003 accurately tracks bottom-water temperatures. A new empirical paleotemperature equation for this scallop species relates temperature and $\delta^{18}\text{O}_{\text{shell calcite}}$:

$$t(^{\circ}\text{C}) = 20.00(\pm 0.61) - 3.66(\pm 0.39) \times (\delta^{18}\text{O}_{\text{shell calcite VPDB}} - \delta^{18}\text{O}_{\text{water VSMOW}})$$

The mean absolute accuracy of temperature estimated using this equation is 1.0 °C at temperatures between 20 and 30 °C. Uncertainties regarding the precise timing of CaCO_3 deposition and the actual variations in $\delta^{18}\text{O}_{\text{water}}$ at our study sites probably contribute to this error. Comparison with a previously published empirical paleotemperature equation indicates that *C. radula* calcite is enriched in ^{18}O by ~0.7 ‰ relative to equilibrium. Given the direction of this offset and the lack of correlation between shell growth rate and $\delta^{18}\text{O}_{\text{shell calcite}}$, this disequilibrium is unlikely to be related to kinetic isotope effects. We suggest that this enrichment reflects (1) a relatively low pH in the scallop's marginal extrapallial fluid (EPF), (2) an isotopic signature of the EPF different from that of seawater, or (3) Rayleigh fractionation during the biocalcification process. Relative changes in $\delta^{18}\text{O}_{\text{shell calcite}}$ reflect seawater temperature variability at this location and we suggest that the shell of *C. radula* may be useful as an archive of past seawater temperatures.

27

1. INTRODUCTION

28

29 Paleoclimate archives are important tools for understanding the causes of climate change
30 and for the validation of climate models (Dunbar and Cole, 1999). In most climate models, sea
31 surface temperature (SST) is an important variable because of its correlation with and control of
32 other climate parameters such as atmospheric moisture content and temperature, rainfall, and
33 heat flux. The known spatial heterogeneity of climatic response to changes in radiative forcing
34 suggests a need for well-calibrated paleoclimate records from diverse geographic settings.

35 The oxygen isotope ratio ($^{18}\text{O}/^{16}\text{O}$) of marine biogenic carbonate is controlled by
36 temperature and the oxygen isotope composition of the seawater from which it precipitates
37 (McCrea, 1950; Epstein et al., 1953). Oxygen isotope paleothermometry has been employed in a
38 number of studies of Cenozoic marine molluscs (Krantz et al., 1987; Andreasson and Schmitz,
39 1996; Bice et al., 1996; Andreasson and Schmitz, 1998; Kirby et al., 1998; Andreasson and
40 Schmitz, 2000; Hickson et al., 2000; Tripathi et al., 2001; Dutton et al., 2002) because their shells
41 grow by periodic accretion of calcite or aragonite (Pannela and McClintock, 1968). This
42 characteristic provides a means of assigning calendar dates to each successive band of accreted
43 shell material, assuming that the periodicity of accretion is known. Using improved micro-
44 sampling and micro-analytical techniques, several recent studies have demonstrated that rapidly
45 growing bivalve mollusc shells contain high resolution proxy records of seawater temperature
46 (Kennedy et al., 2001; Elliot et al., 2003; Chauvaud et al., 2005).

47 In this study, we compare in-situ instrumental seawater temperature with the oxygen
48 isotope composition of shell calcite from six juvenile scallops (*Comptopallium radula*, L., 1758)
49 from the southwest lagoon of New Caledonia (Fig. 1a). *C. radula* is a large ($H_{\infty} = 92.4$ mm;
50 Lefort, 1994) sedentary scallop that lives under branching corals or on coralline fragment beds,
51 generally between 0.5 and 5 m depth, in the tropical Indo-West Pacific Ocean. As in many other
52 scallop species, the shell surface of *C. radula* is textured with concentric striae (Fig. 1b).
53 Marking experiments using calcein fluorescent dye have demonstrated that one stria is formed
54 every two days (Thébault et al., 2006). We have now measured the oxygen isotope composition

55 of carbonate samples collected along shell growth transects to develop an empirical temperature
56 equation which is then compared with some previous $\delta^{18}\text{O}$:temperature relationships calibrated
57 for inorganically precipitated calcite and other molluscs.

58 Most previous paleotemperature records from this region are derived from elemental and
59 isotopic ratios in scleractinian corals (Beck et al., 1992; Quinn et al., 1996a,b; Quinn et al.,
60 1998; Quinn and Sampson, 2002; Watanabe et al., 2003; Corrège et al., 2004; Kilbourne et al.,
61 2004). Our dataset contributes to the relatively small number of oxygen isotope studies on
62 scallop species (Krantz et al., 1984; Krantz et al., 1987; Tan et al., 1988; Hickson et al., 2000;
63 Owen et al., 2002a,b; Chauvaud et al., 2005) and allows the evaluation of the potential of *C.*
64 *radula* for paleoclimatic studies.

65

66

2. METHODS

67

2.1. Study area

69

70 New Caledonia is located in the southwest Pacific Ocean, between 19-23°S and
71 163-168°E (Fig. 2). The main island, Grande Terre, is surrounded by an 1100 km long barrier
72 reef. The southwest lagoon covers 2066 km² and has an average depth of 21 m. Our study sites
73 near Nouméa are Sainte-Marie Bay (22°18'22"S, 166°28'89"E) and Koutio Bay (22°13'45"S,
74 166°25'33"E). Both sites are shallow (< 5 m depth) with muddy sandy sediment. Bottom-water
75 temperatures and salinities were measured from August 7, 2002 to August 1, 2003.
76 Temperatures were recorded hourly using a EBRO EBI-85A thermal probe fixed to a bottom
77 mooring (accuracy ± 0.1 °C). Salinity (average of the first meter of the water column above the
78 seafloor) was measured weekly using a SeaBird SBE19 CTD profiler, and is reported using the
79 Practical Salinity Scale. Salinity data were interpolated linearly to obtain daily values.

80 Because salinity and $\delta^{18}\text{O}_{\text{water}}$ are positively correlated (Craig and Gordon, 1965), the
81 oxygen isotope composition of water was measured at twelve sampling sites along a salinity
82 gradient in the Dumbéa River (Fig. 2) at the beginning of the 2003 dry season (normal river

83 flow). The $\delta^{18}\text{O}_{\text{water}}$ analyses were performed using a modification of the standard $\text{CO}_2\text{-H}_2\text{O }^{18}\text{O}$
84 isotope equilibration technique (Epstein and Mayeda, 1953). For each sample, 2.4 mL of water
85 were equilibrated for 6 h in a reaction vessel with CO_2 at 880 mbar and 21 °C. A cold trap at
86 -80 °C was used to remove water and the resultant CO_2 was frozen onto a cold finger prior to
87 analysis on a Europa SIRA II dual-inlet isotope ratio mass spectrometer. The internal standard
88 used was North Sea Water ($\delta^{18}\text{O} = -0.20 \text{‰}$ VSMOW). Analytical precision was 0.06 ‰ (1 σ).
89 All samples were run in duplicate and data are reported in ‰ with respect to VSMOW. Salinity
90 was measured using a Guildline 8410A Portasal inductive salinometer (accuracy ± 0.002),
91 calibrated with IAPSO Standard Seawater (Ocean Scientific International Ltd., Petersfield, UK).
92 Three samples were measured in triplicate with an average standard deviation of 0.008.

93

94 **2.2. Scallop sampling, preparation, and analysis**

95

96 *Comptopallium radula* grows rapidly, especially during the first two years of life (Lefort,
97 1994). After sexual maturity is achieved during the third year (Lefort and Clavier, 1994), the
98 annual shell growth rate drops. For this study only juvenile scallops were analysed because they
99 have the largest annual increase in shell size (compared with mature specimens) and provide the
100 highest temporal resolution in carbonate records.

101 Six live juvenile *C. radula* specimens (maximum shell height = 69.2 mm) were collected
102 by SCUBA diving at the beginning of the 2003 cool season. In Sainte-Marie Bay, shell SM1
103 was collected on June 23, shell SM2 on July 1, and shell SM3 on July 13. In Koutio Bay, shell
104 BK1 was harvested on May 21, shell BK2 on June 14, and shell BK3 on July 2. After
105 collection, the scallops were immediately killed and their shells cleaned by soaking in 90 %
106 acetic acid for 45-60 s to remove bio-fouling, and then rinsed with distilled water and air-dried.

107 Shell samples ($n = 225$; 34 to 40 samples per shell) for isotopic analyses were collected
108 (using a hand-held micro-drill equipped with a 0.6-mm engraving bit) along a transect line
109 perpendicular to the striae, from the umbo to the ventral margin (Fig. 1b). Drilling was
110 restricted to the ridges of the striae to ensure that shell material was not cross-contaminated by

111 mineralogically different layers of CaCO₃. Because the distance between two successive striae
112 is not constant, each sample contained material from 2 to 5 striae (average = 2.3 striae/sample),
113 and was separated from the next sample by 1 to 3 striae (average = 1.2 striae). Given the 2-day
114 periodicity of striae formation (Thébault et al., 2006), this sampling scheme means that each
115 sample corresponds approximately to 7 days of growth.

116 Aliquots of shell calcite weighing between 32 and 212 μg (mean = 88 μg) were acidified
117 in 100 % phosphoric acid at 70 °C for 470 s and analyzed using an automated Finnigan MAT
118 Kiel III carbonate device coupled to a Finnigan MAT 252 isotope ratio mass spectrometer at
119 Stanford University. Shell isotopic data are expressed in conventional delta (δ) notation (Epstein
120 et al., 1953) relative to the VPDB standard. A total of 25 samples of the international isotopic
121 reference standard NBS-19 (mean weight of standard aliquots = 83 μg) and 15 samples of the
122 Stanford Isotope Lab Standard SLS-1 (mean weight = 84 μg) were analyzed with the scallops
123 and yielded a reproducibility (1σ) of 0.049 ‰ VPDB (NBS-19) and 0.051 ‰ VPDB (SLS-1)
124 for δ¹⁸O, and 0.029 ‰ VPDB (NBS-19) and 0.035 ‰ VPDB (SLS-1) for δ¹³C.

125 A date of formation was assigned to each sample drilled from all shells (except SM2) by
126 backdating from the outer most stria (i.e., harvest date), based on the 2-day periodicity of striae
127 formation in juvenile *C. radula* (Thébault et al., 2006). A different method was used for shell
128 SM2 because of a clearly visible hiatus in shell growth on its external surface. This growth
129 hiatus corresponds to a period during which shell growth ceased. The date of growth cessation
130 and the duration of the interval of zero growth were, however, unknown. The method we used
131 for shell SM2 is based on the very small inter-individual variability of δ¹⁸O_{shell calcite} profiles in *C.*
132 *radula*. First, all samples collected between the ventral margin and the growth hiatus were dated
133 using the method described for the 5 other shells (time-anchored part of the SM2 δ¹⁸O profile -
134 absolute chronology). Then, each sample collected between the growth hiatus and the umbo was
135 dated in relation to the next one, based on the periodicity of striae formation (time-unanchored
136 part of the SM2 δ¹⁸O profile - relative chronology). Finally, this time-unanchored part of the
137 SM2 δ¹⁸O profile was time correlated with the mean δ¹⁸O profile calculated from the other 5

138 shells, allowing us to determine the absolute chronology of the dataset (synchronization
139 involved the maximization of the correlation coefficient between these two datasets). This
140 method permits the estimation of the date of growth cessation as well as the duration of the
141 interval of zero growth.

142 An estimate of shell growth rate, based on the periodicity of striae formation, was made
143 for each shell by measuring distances between successive striae (growth increment width) using
144 an image analysis technique described in detail by Chauvaud et al. (1998). The estimated
145 growth rates are expressed in $\mu\text{m } 2\text{d}^{-1}$. In this paper, we define “shell growth rate” as the
146 dorso-ventral linear extension of the shell per unit time. Since this does not take into account
147 ontogenetic changes in shell thickness, growth rate is likely to differ from absolute calcification
148 rate (see Gillikin et al. (2005) for a helpful discussion).

149 The outer layer of scallop shells was found to be composed of pure foliated calcite (Roux
150 et al., 1990; Barbin et al., 1991). Nevertheless, we checked the mineralogy of the striae we
151 sampled using an X-ray powder diffractometer equipped with an INEL curved
152 position-sensitive detector (CPS120) and a graphite monochromator, using $\text{CoK}_{\alpha 1}$ radiation at
153 35 mA and 30 kV.

154

155 **2.3. Calibration of the $\delta^{18}\text{O}$:temperature relationship**

156

157 As described in section 2.2, the $\delta^{18}\text{O}$ value of each sample represents an average of
158 ~ 5 days growth (~ 2.3 striae). To match this isotopic time averaging, 5-day moving averages of
159 temperature and interpolated weekly salinity measurements were calculated for the calibration.
160 Ordinary Least Squares (OLS) regression was used to examine the $\delta^{18}\text{O}$:temperature
161 relationship, by expressing $\delta^{18}\text{O}$ as the isotopic difference between shell calcite and seawater:

162

$$163 \quad t = A + B \times (\delta^{18}\text{O}_{\text{shell calcite}} - \delta^{18}\text{O}_{\text{water}}), \quad (1)$$

164

165 where t is temperature ($^{\circ}\text{C}$), A and B are constants, and $\delta^{18}\text{O}_{\text{shell calcite}}$ and $\delta^{18}\text{O}_{\text{water}}$ are expressed
166 in ‰ relative to VPDB and VSMOW, respectively. A “comparison of regression lines”
167 procedure (Statgraphics Centurion XV statistical software) was used to test whether there were
168 significant differences between the slopes of the OLS regressions calculated for each of the six
169 shells, and between the slopes of the OLS regressions calculated for each of the two study sites.

170 This relationship was then compared to previous paleotemperature equations established
171 for other calcitic molluscs (Epstein et al., 1953; Owen et al., 2002a; Chauvaud et al., 2005) and
172 for inorganically precipitated calcite (Kim and O’Neil, 1997). In the equation of Epstein et al.
173 (1953), later modified by Craig (1965), both calcite and water oxygen isotope data are relative
174 to the same working standard of the mass spectrometer used in the early days at the University
175 of Chicago, i.e., CO_2 from PDB. Water analyses normalized to the VSMOW scale and
176 carbonates normalized to the VPDB scale cannot be used in this equation. However, it was
177 rewritten by Sharp (2006) in a form appropriate for calcite and water oxygen isotope data
178 expressed relative to VPDB and VSMOW, respectively. The equation of Owen et al. (2002a)
179 was also rewritten in a form suitable for comparison, considering the whole of their dataset (i.e.,
180 31 data points instead of 22 in their equation). To allow comparison with our linear relationship,
181 the equation of Kim and O’Neil (1997) was modified from the form $10^3 \ln \alpha = A(10^3 T^{-1}) + B$,
182 and was approximated by a least squares linear regression following conversion of their
183 $\delta^{18}\text{O}_{\text{calcite}}$ data to the VPDB scale. Calcite oxygen isotope data reported on the VSMOW scale in
184 their study were first corrected (+0.25 ‰) to account for differences between the acid
185 fractionation factor they used (1.01050) and the one commonly accepted for the reaction of
186 carbonate with H_3PO_4 at 25°C (1.01025). These data were then converted to the VPDB scale
187 using the equation of Coplen et al. (1983). The coefficients of these four paleotemperature
188 equations are reported in Table 1.

189

190

3. RESULTS

191

3.1. Hydrologic survey

193

194 From August 2002 to August 2003, the average daily bottom-water temperature ranged
195 from 20.4 to 29.3 °C in Sainte-Marie Bay, and from 20.1 to 29.7 °C in Koutio Bay. The mean
196 diurnal temperature range was 0.6 °C in Sainte-Marie Bay and 0.9 °C in Koutio Bay, with
197 maximum amplitudes of 1.7 and 1.9 °C, respectively. Bottom-water salinity ranged from 34.73
198 to 36.18 in Sainte-Marie Bay, and from 33.43 to 36.52 in Koutio Bay. The water oxygen isotope
199 composition showed a linear co-variation with salinity over the range 2.33-34.68. The
200 relationship between $\delta^{18}\text{O}_{\text{water}}$ and salinity based on a least squares regression equation ($n = 12$,
201 $r^2 = 0.999$, $p < 0.001$) was:

202

$$203 \quad \delta^{18}\text{O}_{\text{water VSMOW}} = 0.168(\pm 0.003) S - 5.068(\pm 0.08), \quad (2)$$

204

205 Quoted errors on the slope and intercept are the 95 % confidence intervals. Extrapolating this
206 linear relationship to a salinity of 36.52 yields a $\delta^{18}\text{O}_{\text{water}}$ annual range of 0.24 ‰ in Sainte-
207 Marie Bay and 0.52 ‰ in Koutio Bay.

208

209 3.2. Mineralogy, shell growth rate and $\delta^{18}\text{O}_{\text{shell calcite}}$

210

211 X-ray diffractograms obtained from powder samples of the shell of *C. radula*
212 unambiguously indicated that striae are composed of calcite. Nevertheless, as XRD is a bulk
213 detection method, we cannot unequivocally state that striae do not contain small amounts of
214 aragonite or magnesium carbonate.

215 The oxygen isotope composition of shell calcite, shell growth rate estimates, and
216 bottom-water temperature are superimposed for each shell in Fig. 3. For all specimens, except
217 SM2, it was not possible to reconstruct growth curves for portions of the shells accreted before

218 August 2002 because of striae abrasion in the oldest parts of the shells. The average shell
219 growth rate was $263 \mu\text{m } 2\text{d}^{-1}$ with maximum values on the order of $450 \mu\text{m } 2\text{d}^{-1}$. There is little
220 similarity between the six growth rate profiles, and no clear seasonal cycle of growth.
221 Moreover, the isotopic record from shell SM2 indicates a growth stop for ca. 2.5 months during
222 the Summer of 2002-2003.

223 The oxygen isotope composition of shell calcite ranged from -1.47 to 0.28 ‰ VPDB (Fig.
224 3). Isotopic profiles of the six shells show similar variations in 2002-2003. In order to determine
225 the influence of temperature, salinity and shell growth rate on $\delta^{18}\text{O}_{\text{shell calcite}}$, the $\delta^{18}\text{O}$ data were
226 fit to a multivariate model of these variables (Table 2). Considering that the p -value for shell
227 growth rate was 0.365 (i.e., $p > 0.01$), this term was not statistically significant and the model
228 was therefore simplified. The best multiple linear regression model incorporated only salinity
229 and temperature. In this model, however, salinity explained only 0.46 % of the variation in
230 $\delta^{18}\text{O}_{\text{shell calcite}}$. Our model also revealed the existence of a statistically significant effect of the
231 interaction "temperature*salinity".
232

233 3.3. Calibration of the paleotemperature equation

234

235 To develop a paleotemperature equation, we used *C. radula* $\delta^{18}\text{O}_{\text{shell calcite}}$, and 5-day
236 moving averages of daily temperature and $\delta^{18}\text{O}_{\text{water}}$ (calculated from salinity measurements). The
237 resulting linear relationship ($n = 225$, $r^2 = 0.609$, $p < 0.001$, Fig. 4) is:

238

$$239 \quad t(^{\circ}\text{C}) = 20.00(\pm 0.61) - 3.66(\pm 0.39) \times (\delta^{18}\text{O}_{\text{shell calcite VPDB}} - \delta^{18}\text{O}_{\text{water VSMOW}}), \quad (3)$$

240

241 Quoted errors on the slope and intercept are the 95 % confidence intervals. This equation was
242 then used with the $\delta^{18}\text{O}_{\text{shell calcite}}$ values of the six scallops to predict the temperature at which the
243 CaCO_3 samples precipitated. The mean absolute error (MAE) shows the accuracy of the
244 temperature prediction to be 1.0°C .

245 The $\delta^{18}\text{O}$:temperature relationships calculated for each of the six shells are presented in
246 Table 3. All relationships were highly significant ($p < 0.001$), with r^2 ranging from 0.490 to
247 0.764, and MAE ranging from 0.8 to 1.2 °C. The test for comparison of slopes reveals that there
248 is no significant difference between the slopes calculated (1) for each of the six shells ($p =$
249 0.447), (2) for the three shells of Sainte-Marie Bay ($p = 0.589$), and (3) for three shells of
250 Koutio Bay ($p = 0.331$). Moreover, this test shows that the slope of the $\delta^{18}\text{O}$:temperature
251 relationship is not significantly different for the two study sites ($p = 0.127$). These results
252 indicate that each specimen preserved similar information, a strong argument in support of the
253 validity of this proxy.

254 The *C. radula* $\delta^{18}\text{O}$:temperature relationship predicts higher temperatures relative to
255 estimates from paleotemperature equations commonly used over the range 20-30 °C (Fig. 5).
256 Our $\delta^{18}\text{O}_{\text{shell calcite}}$ data lie above the equilibrium line (as defined by the equation of Kim and
257 O'Neil (1997) for $[\text{HCO}_3^-] = 5 \text{ mM}$) by, on average, 0.73 ‰, equivalent to a temperature
258 differential of about -3.6 °C. The slope of our equation compares favourably with the slopes of
259 the relationships calibrated by Owen et al. (2002a) and Chauvaud et al. (2005) on the Great
260 Scallop *Pecten maximus* (tests for comparison of slopes: $p = 0.229$ and 0.903, respectively). It
261 is, however, statistically different from the slope of Kim and O'Neil (1997) equation ($p <$
262 0.001).

263

264

4. DISCUSSION

265

4.1. Accuracy and limits of the temperature prediction

267

268 Using radioisotope measurements in the shell of the scallop, *Argopecten irradians*,
269 Wheeler et al. (1975) found that the rate of mineral deposition was lower in the evening than at
270 midday. Moreover, the timing of striae formation in this species was shown to be influenced by
271 the photoperiod, with striae forming primarily in late afternoon and evening (Wrenn, 1972).
272 Nothing is known about the timing of this process in *Comptopallium radula*. Although the time

273 resolution of our oxygen isotope analyses is high (each $\delta^{18}\text{O}_{\text{shell calcite}}$ value represents an average
274 of 4.6 days of CaCO_3 precipitation), if calcification does not take place throughout the day then
275 using average daily temperature values for the calibration of the equation can lead to errors as
276 large as $\pm 0.30\text{ }^\circ\text{C}$ in Sainte-Marie Bay and $\pm 0.45\text{ }^\circ\text{C}$ in Koutio Bay. The sum of errors
277 associated with the diurnal temperature amplitude, our 5-day averaging procedure, and the
278 accuracy of the thermal probe ($\pm 0.1\text{ }^\circ\text{C}$), can explain nearly half ($0.5\text{ }^\circ\text{C}$) of the $1.0\text{ }^\circ\text{C}$
279 uncertainty of the temperature prediction. To proceed further with the use of isotopic signatures
280 as environmental proxies, studies on the timing of CaCO_3 deposition, in addition to better
281 micro-analytical techniques at the scale of individual striae, are necessary.

282 It is also possible that the low sampling frequency for salinity (weekly measurements)
283 was insufficient and induced an unknown amount of error. This is highlighted by a slightly
284 greater mean absolute error for shells harvested from Koutio Bay, a site that experiences greater
285 freshwater inputs and therefore more variable salinity (Table 3). Sea surface salinity (SSS) was
286 measured from 1995 to 2003 at near-daily resolution close to Nouméa (ZoNeCo programme,
287 “Variability of surface thermohaline structures in the New Caledonian Exclusive Economic
288 Zone”). This dataset reveals occasional significant decreases in salinity (down to 28.9) on a sub-
289 weekly basis following storms (characterized by large rainfall and elevated river runoff for 1 or
290 2 days). If such salinity decreases occurred during our study, they may have been missed by our
291 weekly sampling scheme, leading to errors in the estimation of the oxygen isotope composition
292 of seawater used in the calibration equation.

293 A surprising result of our study is the weak influence of salinity on $\delta^{18}\text{O}_{\text{shell calcite}}$ (Table 2).
294 According to Eq. (2), salinity variations should generate annual ranges in $\delta^{18}\text{O}_{\text{water}}$ of 0.24 to
295 0.52 ‰ depending on the study site, which represents 14 to 30 % of the annual range in
296 $\delta^{18}\text{O}_{\text{shell calcite}}$. Therefore, it is astonishing that in our model salinity explains only 0.46 % of the
297 variability of $\delta^{18}\text{O}_{\text{shell calcite}}$. The actual $\delta^{18}\text{O}_{\text{water}}$:salinity relationship, however, may be different
298 from Eq. (2) if salinity variations at our study sites result from a balance between evaporation
299 and precipitation rather than dilution by river water. Moreover, $\delta^{18}\text{O}_{\text{water}}$:salinity relationships

300 can be temporally variable on short timescales (Rohling and Bigg, 1998). Hence, the real annual
301 range in $\delta^{18}\text{O}_{\text{water}}$ may be different from the one calculated from Eq. (2). Temperature is, by far,
302 the dominant factor controlling the shell oxygen isotope composition and this predominance, in
303 addition to the existence of a significant effect of the "temperature*salinity" interaction (Table
304 2), may make it harder to identify the magnitude of a "salinity" effect. Nevertheless, we suggest
305 that salinity-induced change in $\delta^{18}\text{O}_{\text{water}}$ is not a major contributor to the $\delta^{18}\text{O}_{\text{shell calcite}}$ record, as
306 previously proposed by Quinn et al. (1996b) in their study on a massive coral from the
307 southwest lagoon of New Caledonia.

308

309 **4.2. Explanations for the observed fractionation**

310

311 Temperature reconstruction using molluscs is often considered straightforward by virtue
312 of a longstanding assumption that the partitioning of oxygen isotopes between seawater and
313 mollusc shells closely follows the isotopic equilibrium observed between inorganically
314 precipitated calcium carbonate and water. Although this has been confirmed in a number of
315 molluscs (Epstein et al., 1953; Kirby et al., 1998; Surge et al., 2001; Elliot et al., 2003), and in a
316 scallop species (Chauvaud et al., 2005), other studies have reported disequilibrium precipitation
317 of scallop shell calcite (Mitchell et al., 1994; Owen et al., 2002a,b). The variety of fractionation
318 patterns observed implies that species-specific assessments must be completed. This is
319 highlighted by the differences in the equations presented in Fig. 5. Discrepancies between
320 mollusc records and their interpretations often arise from a lack of knowledge of the basic
321 biology and ecology (growth rate, seasonal timing, and duration of growth) of the molluscan
322 species used as environmental recorders.

323 We compared our $\delta^{18}\text{O}_{\text{shell calcite}}$ values with those predicted by the Kim and O'Neil (1997)
324 empirical equation, which is the most recent approximation for equilibrium partitioning of
325 oxygen isotopes between inorganic calcite and seawater. Our results indicate that *C. radula*
326 calcite is enriched in ^{18}O by $\sim 0.73\text{‰}$ with respect to inorganic calcite precipitated in
327 equilibrium with water. Deviation from isotopic equilibrium in biogenic carbonates has been

328 explained historically in terms of “vital effects” (Urey, 1947) which include a combination of
329 kinetic and metabolic effects (McConnaughey, 1989). Kinetic effects, inferred from a
330 simultaneous depletion in ^{18}O and ^{13}C and a linear correlation between skeletal $\delta^{18}\text{O}$ and $\delta^{13}\text{C}$,
331 have been observed at high calcification rates in the carbonate skeletons of some organisms
332 (McConnaughey, 1989). A weak but statistically significant $\delta^{18}\text{O}:\delta^{13}\text{C}$ linear relationship is
333 observed when data from the 6 scallops are pooled ($n = 225$, $r^2 = 0.206$, $p < 0.001$; Fig. 6).
334 However, if kinetic effects associated with high *C. radula* calcification rates had occurred, we
335 would have measured lower $\delta^{18}\text{O}$ values than predicted by the Kim and O’Neil (1997) equation.
336 In addition, no significant relationship was found between $\delta^{18}\text{O}_{\text{shell calcite}}$ and shell growth rate
337 (Table 2).

338 Kim and O’Neil (1997) observed that the extent of isotopic fractionation between water
339 and calcite increased with increasing initial concentration of bicarbonate ions at any given
340 temperature. They concluded that calcites precipitated from solutions of varying $[\text{HCO}_3^-]$ were
341 forming out of oxygen isotopic equilibrium with water since there should be only one
342 equilibrium fractionation factor between calcite and water at any temperature. Spero et al.
343 (1997) have shown that $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ values of calcitic shells of living planktonic foraminifera
344 decrease as seawater $[\text{CO}_3^{2-}]$ (or pH) increases. Zeebe (1999) suggested that the disequilibrium
345 precipitation described by Kim and O’Neil (1997) may be explained by multiple equilibrium
346 fractionations at a constant temperature but different pH values. Zeebe (1999) estimated that the
347 pH of the solution resulting in the equation of Kim and O’Neil (1997) was 7.8 and that an
348 increase in seawater pH by 0.1 unit produces a decrease of 0.11 ‰ in $\delta^{18}\text{O}_{\text{calcium carbonate}}$.

349 Two other recent studies found that the $\delta^{18}\text{O}_{\text{shell calcite}}$ of the scallop *Pecten maximus*
350 exhibited enrichment relative to equilibrium (as determined by the Kim and O’Neil (1997)
351 equation) in both laboratory (+0.6 ‰; Owen et al., 2002a) and field experiments (+0.4 ‰;
352 Owen et al., 2002b). Our observed +0.73 ‰ enrichment is in good agreement with results of
353 these two studies. Using Zeebe’s model, the fractionation we measured in *C. radula* may be
354 explained by a pH of ~7.14 in the extrapallial fluid (EPF) where shell calcification actually
355 takes place. Analyses of marine bivalve EPF have shown its chemistry is significantly different

356 from that of seawater. The pH of EPF was measured in many marine bivalve species, with most
357 values lying between 7.3 and 7.5, i.e., lower than in the external medium (for example, seawater
358 at pH 7.9 to 8.2; Crenshaw, 1972; Wada and Fujinuki, 1976). This lowered pH is consistent
359 with biomineralization models that assume the EPF is isolated from ambient seawater and that
360 exchanges between this compartment and the external medium through the periostracum are
361 limited, such as in the general model of molluscan shell calcification proposed by Wilbur and
362 Saleuddin (1983). Therefore, the enrichment observed in the shell of *C. radula* could be related
363 to low pH in the EPF compared to the pH in the experiment of Kim and O'Neil (1997), more
364 than to vital effects.

365 According to Kim et al. (2006), however, Zeebe's model may be invalid and the isotopic
366 fractionation between carbonate (aragonite and witherite) and water is independent of pH.
367 Therefore, we suggest that the offset from equilibrium we observed may result from an isotopic
368 signature of the EPF different from that of seawater, or by some kind of Rayleigh fractionation.
369 The latter process occurs in a closed system or a finite reservoir when a chemical reaction
370 fractionates isotopes and the reaction products are removed from the system or do not back-
371 react. This results in a shift of the oxygen isotope composition of both the reactant and the
372 product of the reaction. Rayleigh fractionation has been well described for changes in the $\delta^{18}\text{O}$
373 of water and vapour during evaporation where the vapour is continuously removed (i.e., isolated
374 from the water) with a constant fractionation factor (Kendall and Caldwell, 1998). This process
375 may occur during biocalcification of the shell of *C. radula* as (1) exchanges between the
376 external medium and the extrapallial compartment are limited (semi-closed system; see Wilbur
377 and Saleuddin, 1983), limiting the pool of HCO_3^- ions required by the reaction, and (2) the
378 product of this reaction (i.e., calcite) does not back-react. If the effects of Rayleigh fractionation
379 manifest themselves in the oxygen isotope system, they will result in ^{18}O enrichment in both the
380 HCO_3^- reservoir and the precipitated calcite, as previously suggested by Mickler et al. (2004) to
381 explain the offset from equilibrium they observed in modern tropical speleothems.

382

383 4.3. Conclusions

384

385 This study highlights the potential use of shells as high resolution archives of seawater
386 temperature in New Caledonia. Our new $\delta^{18}\text{O}$:temperature relationship permits the
387 reconstruction of seasonal SST variations within ± 1.0 °C over the temperature range 20-30 °C.
388 Accuracy could be improved with better knowledge of the timing of striae formation and with
389 salinity measurements at higher temporal resolution. We suggest that an observed 0.73 ‰ offset
390 between the *C. radula* $\delta^{18}\text{O}$:temperature relationship and a recent equation describing isotopic
391 equilibrium in inorganic calcite grown in seawater may be caused by (1) differences in solution
392 pH between the scallop's extrapallial fluid and seawater, (2) an isotopic signature of the EPF
393 different from that of seawater, or (3) Rayleigh fractionation in both the HCO_3^- reservoir and the
394 calcite precipitated from it. These hypotheses remain to be demonstrated following detailed
395 chemical analyses of the EPF.

396 In the past decade, several authors examined geochemical records ($\delta^{18}\text{O}$, Sr/Ca, Mg/Ca,
397 U/Ca) of SST variability in corals from the tropical south west Pacific Ocean (e.g., Kilbourne et
398 al. (2004) and references therein). These long-lived organisms can be used to reconstruct SST
399 variations over several centuries. However, subannual SST reconstructions using corals are
400 problematic because of the absence of clear sub-annual growth bands (Risk and Pearce, 1992).
401 In most high resolution coral studies (e.g., Meibom et al., 2004), a chronology is developed by
402 assuming constant growth rates and measuring distance along a transect, even though corals are
403 known to exhibit highly variable daily growth rates (Risk and Pearce, 1992). In contrast, scallop
404 shells can provide short SST time series (on the order of a few years) with very high temporal
405 resolution (circa-daily), thus providing accurate estimates of the full range of environmental
406 conditions that these organisms experience while growing. Scallops are thus more likely to
407 record high frequency, extreme environmental events, at least as long as the stress induced does
408 not interfere with the scallop's growth. This characteristic is particularly useful for the
409 investigation of coral bleaching events. Moberg et al. (2005) pointed out the need for

410 multi-proxy approaches for accurate reconstruction of past seawater temperature variations, by
411 combining long, low-frequency data sets (such as from corals) with high-frequency information
412 (e.g., from scallop shell data). As a large edible species, ancient *C. radula* specimens are
413 abundant at archaeological sites (J.-C. Galipaud, personal communication), and ancient shells
414 may also be found by coring fossil reef or sand units. In this context, corals and scallops may
415 become complementary tools for SST reconstructions in the tropical southwest Pacific.

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TABLES

Table 1. Summary of some previous $\delta^{18}\text{O}$:temperature relationships calibrated for inorganically precipitated calcite and for calcitic molluscs. Oxygen isotope compositions of calcite (δ_c) and water (δ_w) are expressed relative to VPDB and VSMOW, respectively.

Reference	Source	$t(^{\circ}\text{C}) = A + B (\delta_c - \delta_w) + C (\delta_c - \delta_w)^2$			Temperature range
		<i>A</i>	<i>B</i>	<i>C</i>	
Kim and O'Neil (1997) ^a	Inorganic	14.97	-4.97		10 - 40 °C
Owen et al. (2002a) ^a	Mollusc (<i>Pecten maximus</i>)	17.15	-3.99		10 - 17 °C
Chauvaud et al. (2005)	Mollusc (<i>Pecten maximus</i>)	14.84	-3.75		9 - 18 °C
Sharp (2006) ^b	Molluscs	15.75	-4.30	0.14	7 - 29.5 °C

(a) Rewritten in a form appropriate for comparison

(b) After Epstein et al. (1953) and Craig (1965)

Table 2. Multiple linear regression between *Comptopallium radula* $\delta^{18}\text{O}_{\text{shell calcite}}$, temperature, salinity, and shell growth rate in 2002-2003, considering or not shell growth rate.

	Estimate	Std. error	T	p
<i>Shell growth rate considered</i> ^a				
Intercept	84.66	18.77	4.511	< 0.001
Temperature (t)	-3.200	0.733	-4.363	< 0.001
Salinity (S)	-2.241	0.527	-4.253	< 0.001
Growth rate (GR)	-0.016	0.017	-0.908	0.365
t*S	0.084	0.021	4.056	< 0.001
t*GR	0.0003	0.0001	2.193	0.029
S*GR	0.0003	0.0005	0.548	0.584
<i>Shell growth rate not considered</i> ^b				
Intercept	77.98	18.45	4.227	< 0.001
Temperature (t)	-3.030	0.727	-4.170	< 0.001
Salinity (S)	-2.103	0.522	-4.027	< 0.001
t*S	0.081	0.021	3.937	< 0.001

(a) Multiple r^2 : 0.705; adjusted r^2 : 0.697; F-statistic: 86.68 on 6 and 218 DF; p -value: < 0.001.

(b) Multiple r^2 : 0.694; adjusted r^2 : 0.690; F-statistic: 166.8 on 3 and 221 DF; p -value: < 0.001.

Table 3. Parameters of the $\delta^{18}\text{O}$:temperature relationships (OLS regressions) calculated for each of the six shells separately, then for the shells of each study site separately. Also shown are the p -values resulting from the “comparison of regression lines” procedure.

Model fitting results: $t(^{\circ}\text{C}) = A + B (\delta^{18}\text{O}_{\text{shell calcite VPDB}} - \delta^{18}\text{O}_{\text{water VSMOW}})$							Test for equality of slopes			
Shell	n	p	r^2	A	B	MAE	Source	p	Source	p
SM1	38	< 0.001	0.748	19.45	-4.03	0.8	SM1	0.589	SM1	0.447
SM2	34	< 0.001	0.764	18.70	-4.04	0.8	SM2		SM2	
SM3	40	< 0.001	0.650	19.89	-3.53	0.8	SM3		SM3	
BK1	40	< 0.001	0.490	20.28	-3.86	1.2	BK1	0.331	BK1	
BK2	37	< 0.001	0.655	20.10	-3.73	0.9	BK2		BK2	
BK3	36	< 0.001	0.536	21.42	-2.88	1.0	BK3		BK3	
SM _{pooled}	112	< 0.001	0.718	19.22	-3.95	0.8	SM _{pooled}	0.127		
BK _{pooled}	113	< 0.001	0.539	20.77	-3.37	1.1	BK _{pooled}			

FIGURE CAPTIONS

Fig. 1. a) Photograph of the upper surface of the left valve of *Comptopallium radula*. The maximal growth axis is indicated by the white arrow. b) Image (scanning electron microscopy) of striae taken along the maximal growth axis. These striae have been demonstrated to form with a 2-day periodicity (Thébault et al., 2006). Three shell samples drilled for isotopic analysis can be readily seen. Each sample contains material from two striae and is separated from the next one by two striae.

Fig. 2. Scallop sampling locations in the southwest lagoon of New Caledonia. Dashed line delimits the area of water sampling for $\delta^{18}\text{O}_{\text{water}}$:salinity calibration.

Fig. 3. Variations of $\delta^{18}\text{O}_{\text{shell calcite}}$ (black points), bottom-water temperature (5-day moving average; black line) and shell growth rate (grey area) in the six studied *Comptopallium radula* specimens, from August 2002 to July 2003.

Fig. 4. Relationship between bottom-water temperature ($^{\circ}\text{C}$) and $(\delta^{18}\text{O}_{\text{shell calcite}} - \delta^{18}\text{O}_{\text{water}})$ where $\delta^{18}\text{O}_{\text{shell calcite}}$ and $\delta^{18}\text{O}_{\text{water}}$ are expressed on the VPDB and VSMOW scales, respectively. Also represented are the linear regression model and its equation.

Fig. 5. Comparison of temperature predictions using our new *Comptopallium radula* $\delta^{18}\text{O}$:temperature relationship and previously published paleotemperature equations. The position of our equation with respect to the theoretical equilibrium equation of Kim and O'Neil (1997) indicates that the shell of *Comptopallium radula* is not formed in isotopic equilibrium with seawater.

Fig. 6. Relationship between $\delta^{18}\text{O}_{\text{shell calcite}}$ and $\delta^{13}\text{C}_{\text{shell calcite}}$ of the 6 juvenile scallops (OLS regression: $n = 225$, $r^2 = 0.206$, $p < 0.001$).

Figure 1

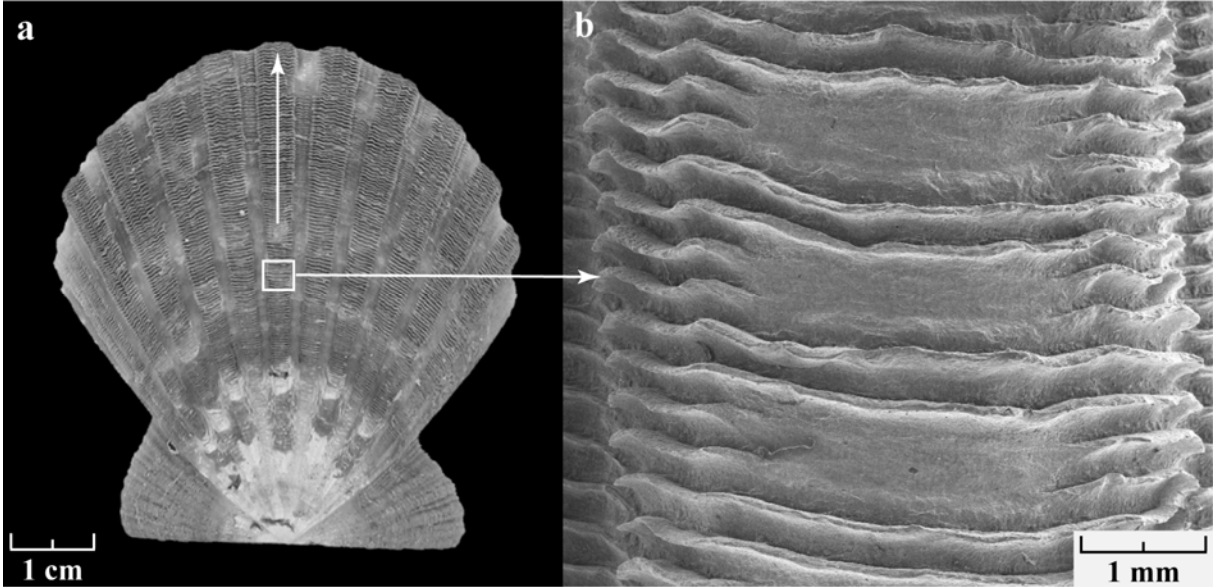


Figure 2

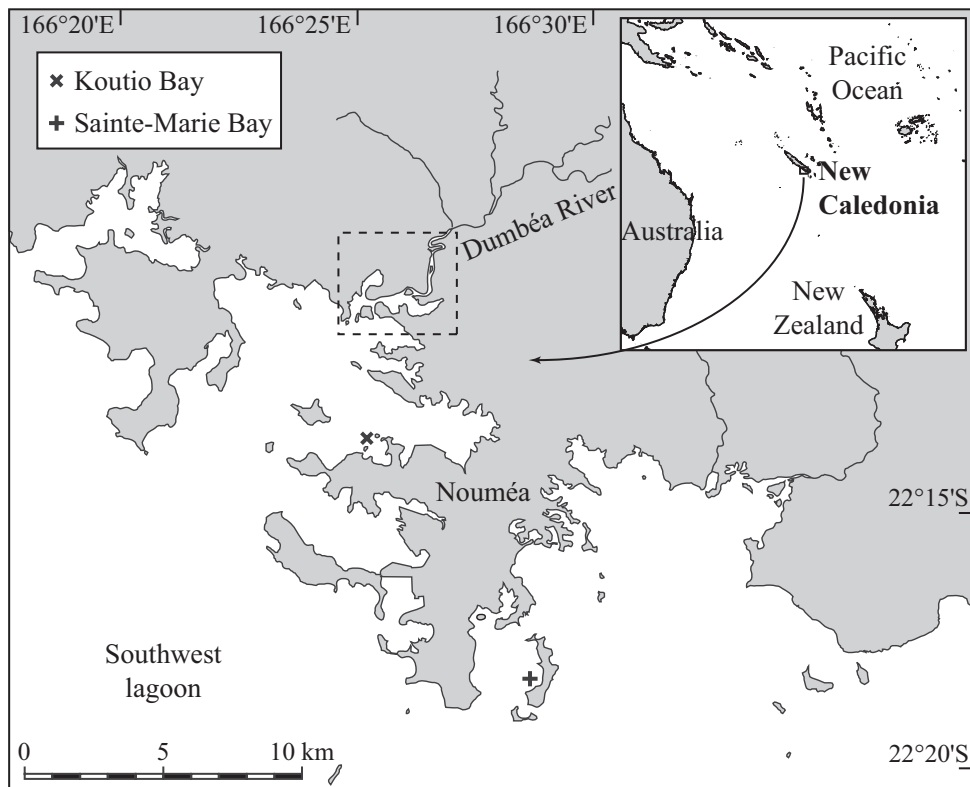


Figure 3

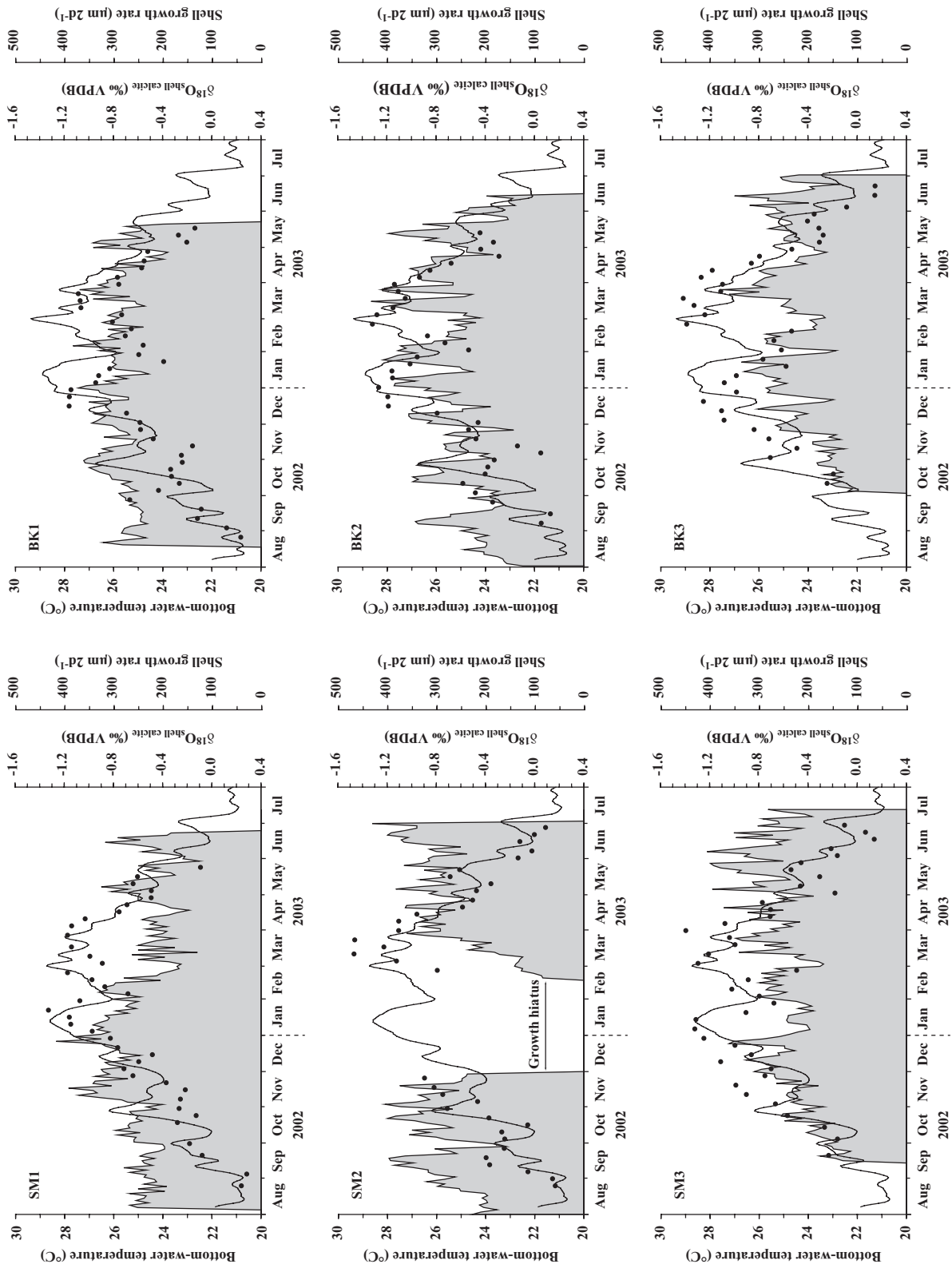


Figure 4

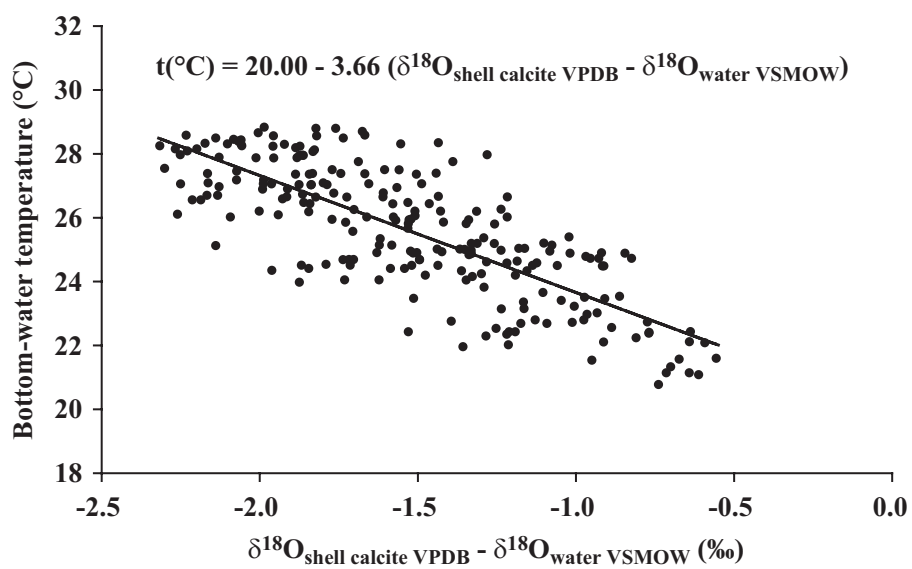


Figure 5

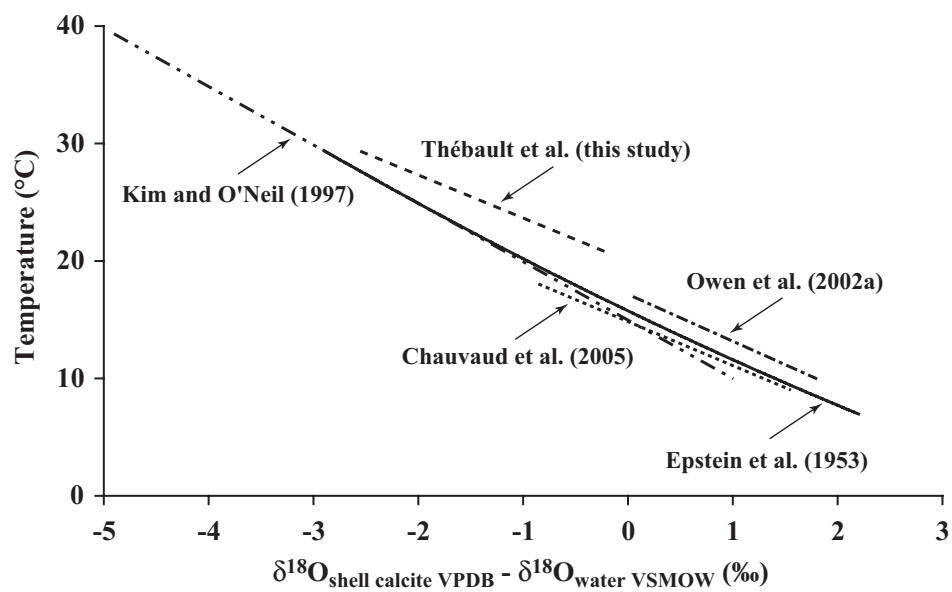


Figure 6

