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

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Abstract

We investigated the oxygen isotope composition (δ18O) 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 (δ18Oshell 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 δ18Oshell calcite:

\[ t(°C) = 20.00(±0.61) - 3.66(±0.39) \times (δ^{18}O_{\text{shell calcite}}_{V_PDB} - δ^{18}O_{\text{water VSMOW}}) \]

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 CaCO3 deposition and the actual variations in δ18Owater at our study sites probably contribute to this error. Comparison with a previously published empirical paleotemperature equation indicates that C. radula is enriched in 18O by ~0.7‰ relative to equilibrium. Given the direction of this offset and the lack of correlation between shell growth rate and δ18Oshell 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 δ18Oshell 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.

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1. Introduction

Paleoclimate archives are important tools for understanding the causes of climate change and for the validation of climate models (Dunbar and Cole, 1999). In most climate models, sea surface temperature (SST) is an important variable because of its correlation with and control of other climate parameters such as atmospheric moisture content and temperature, rainfall, and heat flux. The known spatial heterogeneity of climatic response to changes in radiative forcing suggests a need for well-calibrated paleoclimate records from diverse geographic settings.
The oxygen isotope ratio ($^{18}$O/$^{16}$O) of marine biogenic carbonate is controlled by temperature and the oxygen isotope composition of the seawater from which it precipitates (McCrea, 1950; Epstein et al., 1953). Oxygen isotope paleothermometry has been employed in a number of studies of Cenozoic marine molluscs (Krantz et al., 1987; Andreasson and Schmitz, 1996; Bice et al., 1996; Andreasson and Schmitz, 1998; Kirby et al., 1998; Andreasson and Schmitz, 2000; Hickson et al., 2000; Tripati et al., 2001; Dutton et al., 2002) because their shells grow by periodic accretion of calcite or aragonite (Pannella and MacClintock, 1968). This characteristic provides a means of assigning calendar dates to each successive band of accreted shell material, assuming that the periodicity of accretion is known. Using improved micro-sampling and micro-analytical techniques, several recent studies have demonstrated that rapidly growing bivalve mollusc shells contain high resolution proxy records of seawater temperature (Kennedy et al., 2001; Elliot et al., 2003; Chauvaud et al., 2005).

In this study, we compare in-situ instrumental seawater temperature with the oxygen isotope composition of shell calcite from six juvenile scallops (Comptopallium radula, L., 1758) from the southwest lagoon of New Caledonia (Fig. 1a). *C. radula* is a large ($H_{\infty} = 92.4$ mm; Lefort, 1994) sedentary scallop that lives under branching corals or on coralline fragment beds, generally between 0.5 and 5 m depth, in the tropical Indo-West Pacific Ocean. As in many other scallop species, the shell surface of *C. radula* is textured with concentric striæ (Fig. 1b). Marking experiments using calcein fluorescent dye have demonstrated that one stria is formed every two days (Thébault et al., 2006). We have now measured the oxygen isotope composition of carbonate samples collected along shell growth transects to develop an empirical temperature equation which is then compared with some previous $\delta^{18}$O-temperature relationships calibrated for inorganically precipitated calcite and other molluscs.

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

2. Methods

2.1. Study area

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

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 striæ taken along the maximal growth axis. These striæ 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 striæ and is separated from the next one by two striæ.
Salinity data were interpolated linearly to obtain daily values.

Because salinity and \(^{18}\)O in water are positively correlated (Craig and Gordon, 1965), the oxygen isotope composition of water was measured at twelve sampling sites along a salinity gradient in the Dumbéa River (Fig. 2) at the beginning of the 2003 dry season (normal river flow). The \(^{18}\)O in water analyses were performed using a modification of the standard CO₂–H₂O \(^{18}\)O isotope equilibration technique (Epstein and Mayeda, 1953). For each sample, 2.4 mL of water were equilibrated for 6 h in a reaction vessel with CO₂ at 880 mbar and 21°C. A cold trap at −80°C was used to remove water and the resultant CO₂ was frozen onto a cold finger prior to analysis on a Europa SIRA II dual-inlet isotope ratio mass spectrometer. The internal standard used was North Sea Water (\(^{18}\)O = −0.20‰ VSMOW). Analytical precision was 0.06‰ (1σ). All samples were run in duplicate and data are reported in ‰ with respect to VSMOW. Salinity was measured using a Guildline 8410A Portasal inductive salinometer (accuracy ±0.002), calibrated with IAPSO Standard Seawater (Ocean Scientific International Ltd., Petersfield, UK). Three samples were measured in triplicate with an average standard deviation of 0.008.

2.2. Scallop sampling, preparation, and analysis

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

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

Shell samples (n = 225; 34 to 40 samples per shell) for isotopic analyses were collected (using a hand-held micro-drill equipped with a 0.6-mm engraving bit) along a transect line perpendicular to the striae, from the umbo to the ventral margin (Fig. 1b). Drilling was restricted to the ridges of the striae to ensure that shell material was not cross-contaminated by mineralogically different layers of CaCO₃. Because the distance between two successive striae is not constant, each sample contained material from 2 to 5 striae (average = 2.3 striae/sample), and was separated from the next sample by 1 to 3 striae (average = 1.2 striae). Given the 2-day periodicity of striae formation (Thébault et al., 2006), this sampling scheme means that each sample corresponds approximately to 7 days of growth.

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

A date of formation was assigned to each sample drilled from all shells (except SM2) by backdating from the outermost stria (i.e., harvest date), based on the 2-day periodicity of striae formation in juvenile C. radula (Thébault et al., 2006). A different method was used for shell SM2 because of a clearly visible hiatus in shell growth on its external surface. This growth hiatus corresponds to a period during which shell growth ceased. The date of growth cessation and the duration of the interval of zero growth were, however, unknown. The method we used for shell SM2 is based on the very small inter-individual variability of δ18Oshell calcite profiles in C. radula. First, all samples collected between the ventral margin and the growth hiatus were dated using the method described for the 5 other shells (time-anchored part of the SM2 δ18O profile-absolute chronology). Then, each sample collected between the growth hiatus and the umbo was dated in relation to the next one, based on the periodicity of striae formation (time-anchored part of the SM2 δ18O profile-relative chronology). Finally, this time-unanchored part of the SM2 δ18O profile was time correlated with the mean δ18O profile calculated from the other 5 shells, allowing us to determine the absolute chronology of the dataset (synchronization involved the maximization of the correlation coefficient between these two datasets). This method permits the estimation of the date of growth cessation as well as the duration of the interval of zero growth.

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

The outer layer of scallop shells was found to be composed of pure foliated calcite (Roux et al., 1990; Barbin et al., 1991). Nevertheless, we checked the mineralogy of the striae we sampled using an X-ray powder diffractometer equipped with an INEL curved position-sensitive detector (CPS120) and a graphite monochromator, using CoKα1 radiation at 35 mA and 30 kV.

2.3. Calibration of the δ18O:temperature relationship

As described in section 2.2, the δ18O value of each sample represents an average of ~5 days growth (~2.3 striae). To match this isotopic time averaging, 5-day moving averages of temperature and interpolated weekly salinity measurements were calculated for the calibration. Ordinary Least Squares (OLS) regression was used to examine the δ18O:temperature relationship, by expressing δ18O as the isotopic difference between shell calcite and seawater:

\[
t = A + B \times (\delta^{18}O_{\text{shell calcite}} - \delta^{18}O_{\text{water}}),
\]

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

This relationship was then compared to previous paleotemperature equations established for other calcitic molluscs (Epstein et al., 1953; Owen et al., 2002a; Chauvaud et al., 2005) and for inorganically precipitated calcite (Kim and O’Neil, 1997). In the equation of Epstein et al. (1953), later modified by Craig (1965), both calcite and water oxygen isotope data are relative to the same working standard of the mass spectrometer used in the early days at the University of Chicago, i.e., CO2 from PDB. Water analyses normalized to the VSMOW scale and carbonates normalized to the VPDB scale cannot be used in this equation. However, it was rewritten by Sharp (2006) in a form appropriate for calcite and water oxygen isotope data expressed relative to VPDB and VSMOW, respectively. The equation of Owen et al. (2002a) was also rewritten in a form suitable for comparison, considering the whole of their dataset (i.e., 31 data points instead of 22 in their equation). To allow comparison with our linear relationship, the equation of Kim and O’Neil (1997) was modified from the form 10 ln γ = A(10^8 T^-1) + B, and was approximated by a least squares linear regression following conversion of their δ18Ocalcite data to the VPDB scale. Calcite oxygen isotope data reported on the VSMOW scale in their study were first corrected (+0.25‰) to account for differences between the acid fractionation factor they used (1.01050) and the one commonly accepted for the reaction of carbonate with H3PO4 at 25 °C (1.01025). These data were then converted to the VPDB scale using the equation of Coplen et al. (1983). The coefficients of these four paleotemperature equations are reported in Table 1.

3. Results

3.1. Hydrologic survey

From August 2002 to August 2003, the average daily bottom-water temperature ranged from 20.4 to 29.3 °C in
Sainte-Marie Bay, and from 20.1 to 29.7 °C in Koutio Bay. The mean diurnal temperature range was 0.6 °C in Sainte-Marie Bay and 0.9 °C in Koutio Bay, with maximum amplitudes of 1.7 and 1.9 °C, respectively. Bottom-water salinity ranged from 34.73 to 36.18 in Sainte-Marie Bay, and from 33.43 to 36.52 in Koutio Bay. The water oxygen isotopic composition showed a linear co-variation with salinity over the range 2.33–34.68. The relationship between oxygen isotopes and from 33.43 to 36.52 in Koutio Bay. The water oxygen isotopic composition showed a linear co-variation with salinity over the range 2.33–34.68. The relationship between δ18Owater and salinity based on a least squares regression equation (n = 12, r² = 0.999, p < 0.001) was:

\[
\delta^{18}O_{\text{water VSMOW}} = 0.168(\pm 0.003)S - 5.068(\pm 0.08). \tag{2}
\]

Quoted errors on the slope and intercept are the 95% confidence intervals. Extrapolating this linear relationship to a salinity of 36.52 yields a δ18Owater annual range of 0.24‰ in Sainte-Marie Bay and 0.52‰ in Koutio Bay.

### 3.2. Mineralogy, shell growth rate and δ18Oshell calcite

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

The oxygen isotope composition of shell calcite, shell growth rate estimates, and bottom-water temperature are superimposed for each shell in Fig. 3. For all specimens, except SM2, it was not possible to reconstruct growth curves for portions of the shells accreted before August 2002 because of striae abrasion in the oldest parts of the shells. The average shell growth rate was 263 μm 2d⁻¹ with maximum values on the order of 450 μm 2d⁻¹. There is little similarity between the six growth rate profiles, and no clear seasonal cycle of growth. Moreover, the isotopic record from shell SM2 indicates a growth stop for ca. 2.5 months during the Summer of 2002–2003.

The oxygen isotope composition of shell calcite ranged from −1.47 to 0.28‰ VPDB (Fig. 3). Isotopic profiles of the six shells show similar variations in 2002–2003. In order to determine the influence of temperature, salinity and shell growth rate on δ18Oshell calcite, the δ18O data were fit to a multivariate model of these variables (Table 2). Considering that the p-value for shell growth rate was 0.365 (i.e., p > 0.01), this term was not statistically significant and the model was therefore simplified. The best multiple linear regression model incorporated only salinity and temperature. In this model, however, salinity explained only 0.46% of the variation in δ18Oshell calcite. Our model also revealed the existence of a statistically significant effect of the interaction “temperature×salinity”.

### 3.3. Calibration of the paleotemperature equation

To develop a paleotemperature equation, we used *C. radula* δ18Oshell calcite, and 5-day moving averages of daily temperature and δ18Owater (calculated from salinity measurements). The resulting linear relationship (n = 225, r² = 0.609, p < 0.001, Fig. 4) is:

\[
t(°C) = 20.00(±0.61) - 3.66(±0.39) \times (δ^{18}O_{\text{shell calcite VPDB}} - δ^{18}O_{\text{water VSMOW}}). \tag{3}
\]

Quoted errors on the slope and intercept are the 95% confidence intervals. This equation was then used with the δ18Oshell calcite values of the six scallops to predict the temperature at which the CaCO₃ samples precipitated. The mean absolute error (MAE) shows the accuracy of the temperature prediction to be 1.0 °C.

The δ18O:temperature relationships calculated for each of the six shells are presented in Table 3. All relationships were highly significant (p < 0.001), with r² ranging from 0.490 to 0.764, and MAE ranging from 0.8 to 1.2 °C. The test for comparison of slopes reveals that there is no significant difference between the slopes calculated (1) for each of the six shells (p = 0.447), (2) for the three shells of Sainte-Marie Bay (p = 0.589), and (3) for three shells of Koutio Bay (p = 0.331). Moreover, this test shows that the slope of the δ18O:temperature relationship is not significantly different for the two study sites (p = 0.127). These results indicate that each specimen preserved similar information, a strong argument in support of the validity of this proxy.

The *C. radula* δ18O:temperature relationship predicts higher temperatures relative to estimates from paleotemperature equations commonly used over the range 20–30 °C (Fig. 5). Our δ18Oshell calcite data lie above the equilibrium line (as defined by the equation of Kim and O’Neil (1997) for [HCO₃⁻] = 5 mM) by, on average, 0.73‰.
Table 2
Multiple linear regression between *Comptopallium radula* δ<sup>18</sup>O<sub>shell calcite</sub>, temperature, salinity, and shell growth rate in 2002–2003, considering or not shell growth rate

<table>
<thead>
<tr>
<th></th>
<th>Estimate</th>
<th>Std. error</th>
<th>T</th>
<th>p</th>
</tr>
</thead>
<tbody>
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<td><strong>Shell growth rate considered</strong>&lt;sup&gt;a&lt;/sup&gt;</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Intercept</td>
<td>84.66</td>
<td>18.77</td>
<td>4.511</td>
<td>&lt;0.001</td>
</tr>
<tr>
<td>Temperature (t)</td>
<td>−3.200</td>
<td>0.733</td>
<td>−4.363</td>
<td>&lt;0.001</td>
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<tr>
<td>Salinity (S)</td>
<td>−2.241</td>
<td>0.527</td>
<td>−4.253</td>
<td>&lt;0.001</td>
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<tr>
<td>Growth rate (GR)</td>
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<td>0.017</td>
<td>−0.908</td>
<td>0.365</td>
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<tr>
<td>tS</td>
<td>0.084</td>
<td>0.021</td>
<td>4.056</td>
<td>&lt;0.001</td>
</tr>
<tr>
<td>tGR</td>
<td>0.0003</td>
<td>0.0001</td>
<td>2.193</td>
<td>0.029</td>
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<tr>
<td>SGR</td>
<td>0.0003</td>
<td>0.0005</td>
<td>0.548</td>
<td>0.584</td>
</tr>
<tr>
<td><strong>Shell growth rate not considered</strong>&lt;sup&gt;b&lt;/sup&gt;</td>
<td></td>
<td></td>
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<tr>
<td>Intercept</td>
<td>77.98</td>
<td>18.45</td>
<td>4.227</td>
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<td>Temperature (t)</td>
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<td>−4.170</td>
<td>&lt;0.001</td>
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<td>Salinity (S)</td>
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<tr>
<td>tS</td>
<td>0.081</td>
<td>0.021</td>
<td>3.937</td>
<td>&lt;0.001</td>
</tr>
</tbody>
</table>

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

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

Fig. 3. Variations of δ<sup>18</sup>O<sub>shell calcite</sub> (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 (°C) and ($\delta^{13}$O<sub>shell calcite</sub> - $\delta^{18}$O<sub>water</sub>) where $\delta^{13}$O<sub>shell calcite</sub> and $\delta^{18}$O<sub>water</sub> are expressed on the VPDB and VSMOW scales, respectively. Also represented are the linear regression model and its equation.
Table 3
Parameters of the $\delta^{18}O$: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

<table>
<thead>
<tr>
<th>Shell</th>
<th>$n$</th>
<th>$p$</th>
<th>$r^2$</th>
<th>$A$</th>
<th>$B$</th>
<th>MAE</th>
<th>Source</th>
<th>$p$</th>
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<td>38</td>
<td>&lt;0.001</td>
<td>0.748</td>
<td>19.45</td>
<td>-4.03</td>
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<td>0.8</td>
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<td>SM1</td>
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<tr>
<td>SM3</td>
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<td>19.89</td>
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<td>0.8</td>
<td>SM3</td>
<td>SM3</td>
</tr>
<tr>
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<td>BK1</td>
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<tr>
<td>BK2</td>
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<td>0.9</td>
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<td>BK2</td>
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<tr>
<td>BK3</td>
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<td>&lt;0.001</td>
<td>0.536</td>
<td>21.42</td>
<td>-2.88</td>
<td>1.0</td>
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<td>BK3</td>
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<tr>
<td>SM$_{pooled}$</td>
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<td>&lt;0.001</td>
<td>0.718</td>
<td>19.22</td>
<td>-3.95</td>
<td>0.8</td>
<td>SM$_{pooled}$</td>
<td>SM$_{pooled}$</td>
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<tr>
<td>BK$_{pooled}$</td>
<td>113</td>
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<td>-3.37</td>
<td>1.1</td>
<td>BK$_{pooled}$</td>
<td>BK$_{pooled}$</td>
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</tbody>
</table>

Fig. 5. Comparison of temperature predictions using our new Comptopallium radula $\delta^{18}O$: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.

equivalent to a temperature differential of about $-3.6$ °C. The slope of our equation compares favourably with the slopes of the relationships calibrated by Owen et al. (2002a) and Chauvaud et al. (2005) on the Great Scallop Pecten maximus (tests for comparison of slopes: $p = 0.229$ and $0.903$, respectively). It is, however, statistically different from the slope of Kim and O’Neil (1997) equation ($p < 0.001$).

4. Discussion

4.1. Accuracy and limits of the temperature prediction

Using radioisotope measurements in the shell of the scallop, Argopecten irradians, Wheeler et al. (1975) found that the rate of mineral deposition was lower in the evening than at midday. Moreover, the timing of striae formation in this species was shown to be influenced by the photoperiod, with striae forming primarily in late afternoon and evening (Wrenn, 1972). Nothing is known about the timing of this process in C. radula. Although the time resolution of our oxygen isotope analyses is high (each $\delta^{18}O_{shell} \text{calcite}$ value represents an average of 4.6 days of CaCO$_3$ precipitation), if calcification does not take place throughout the day then using average daily temperature values for the calibration of the equation can lead to errors as large as $\pm 0.30$ °C in Sainte-Marie Bay and $\pm 0.45$ °C in Koutio Bay. The sum of errors associated with the diurnal temperature amplitude, our 5-day averaging procedure, and the accuracy of the thermal probe ($\pm 0.1$ °C), can explain nearly half (0.5 °C) of the 1.0 °C uncertainty of the temperature prediction. To proceed further with the use of isotopic signatures as environmental proxies, studies on the timing of CaCO$_3$ deposition, in addition to better micro-analytical techniques at the scale of individual striae, are necessary.

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

A surprising result of our study is the weak influence of salinity on $\delta^{18}O_{shell} \text{calcite}$ (Table 2). According to Eq. (2), salinity variations should generate annual ranges in $\delta^{18}O_{water}$ of 0.24–0.52‰ depending on the study site, which represents 14–30% of the annual range in $\delta^{18}O_{shell} \text{calcite}$. Therefore, it is astonishing that in our model salinity explains only 0.46% of the variability of $\delta^{18}O_{shell} \text{calcite}$. The actual $\delta^{18}O_{water}$:salinity relationship, however, may be different from Eq. (2) if salinity variations at our study sites result from a balance between evaporation and precipita-
tion rather than dilution by river water. Moreover, δ¹⁸O<sub>water</sub>;salinity relationships can be temporally variable on short timescales (Rohling and Bigg, 1998). Hence, the real annual range in δ¹⁸O<sub>water</sub> may be different from the one calculated from Eq. (2). Temperature is, by far, the dominant factor controlling the shell oxygen isotope composition and this predominance, in addition to the existence of a significant effect of the “temperature=salinity” interaction (Table 2), may make it harder to identify the magnitude of a “salinity” effect. Nevertheless, we suggest that salinity-induced change in δ¹⁸O<sub>water</sub> is not a major contributor to the δ¹⁸O<sub>shell calcite</sub> record, as previously proposed by Quinn et al. (1996b) in their study on a massive coral from the southwest lagoon of New Caledonia.

4.2. Explanations for the observed fractionation

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

We compared our δ¹⁸O<sub>shell calcite</sub> values with those predicted by the Kim and O’Neil (1997) empirical equation, which is the most recent approximation for equilibrium partitioning of oxygen isotopes between inorganic calcite and seawater. Our results indicate that C. radula calcite is enriched in ¹⁸O by ~0.73‰<sub>sw</sub> with respect to inorganic calcite precipitated in equilibrium with water. Deviation from isotopic equilibrium in biogenic carbonates has been explained historically in terms of “vital effects” (Urey, 1947) which include a combination of kinetic and metabolic effects (McConnaughey, 1989). Kinetic effects, inferred from a simultaneous depletion in ¹⁸O and ¹³C and a linear correlation between skeletal δ¹⁸O and δ¹³C, have been observed at high calcification rates in the carbonate skeletons of some organisms (McConnaughey, 1989). A weak but statistically significant δ¹⁸O<sub>shell calcite</sub> versus δ¹³C<sub>shell calcite</sub> linear relationship is observed when data from the 6 scallops are pooled (n = 225, r² = 0.206, p < 0.001; Fig. 6). However, if kinetic effects associated with high C. radula calcification rates had occurred, we would have measured lower δ¹⁸O values than predicted by the Kim and O’Neil (1997) equation. In addition, no significant relationship was found between δ¹⁸O<sub>shell calcite</sub> and shell growth rate (Table 2).

Kim and O’Neil (1997) observed that the extent of isotopic fractionation between water and calcite increased with increasing initial concentration of bicarbonate ions at any given temperature. They concluded that calcites precipitated from solutions of varying [HCO₃⁻] were forming out of oxygen isotopic equilibrium with water since there should be only one equilibrium fractionation factor between calcite and water at any temperature. Spero et al. (1997) have shown that δ¹³C and δ¹⁸O values of calcitic shells of living planktonic foraminifera decrease as seawater [CO₂⁻₃] (or pH) increases. Zeebe (1999) suggested that the disequilibrium precipitation described by Kim and O’Neil (1997) may be explained by multiple equilibrium fractionations at a constant temperature but different pH values. Zeebe (1999) estimated that the pH of the solution resulting in the equation of Kim and O’Neil (1997) was 7.8 and that an increase in seawater pH by 0.1 unit produces a decrease of 0.11‰<sub>sw</sub> in δ¹⁸O<sub>calcium carbonate</sub>.

Two other recent studies found that the δ¹⁸O<sub>shell calcite</sub> of the scallop Pecten maximus exhibited enrichment relative to equilibrium (as determined by the Kim and O’Neil (1997) equation) in both laboratory (+0.6‰<sub>sw</sub>; Owen et al., 2002a) and field experiments (+0.4‰<sub>sw</sub>; Owen et al., 2002b). Our observed +0.73‰<sub>sw</sub> enrichment is in good agreement with results of these two studies. Using Zeebe’s model, the fractionation we measured in C. radula may be explained by a pH of ~7.14 in the extrapallial fluid (EPF) where shell calcification actually takes place. Analyses of marine bivalve EPF have shown its chemistry is significantly different from that of seawater. The pH of EPF was measured in many marine bivalve species, with most values lying between 7.3 and 7.5, i.e., lower than in the external medium (for example, seawater at pH 7.9–8.2; Crenshaw, 1972; Wada and Fujinuki, 1976). This lowered pH is consistent with biomineralization models that assume the EPF is isolated from ambient seawater and that exchanges between this compartment and the external

![Graph](image-url)
medium through the periostracum are limited, such as in the
general model of molluscan shell calcification proposed by
Wilbur and Saleuddin (1983). Therefore, the enrichment
observed in the shell of C. radula could be related to low
pH in the EPF compared to the pH in the experiment of
Kim and O’Neill (1997), more than to vital effects.

According to Kim et al. (2006), however, Zeebe’s model
may be invalid and the isotopic fractionation between car-
bonate (aragonite and witherite) and water is independent
of pH. Therefore, we suggest that the offset from equilibri-
um we observed may result from an isotopic signature of
the EPF different from that of seawater, or by some kind
of Rayleigh fractionation. The latter process occurs in a
closed system or a finite reservoir when a chemical reaction
fractionates isotopes and the reaction products are re-
moved from the system or do not back-react. This results
in a shift of the oxygen isotope composition of both the
reactant and the product of the reaction. Rayleigh fraction-
ation has been well described for changes in the δ18O of
water and vapour during evaporation where the vapour
is continuously removed (i.e., isolated from the water) with
a constant fractionation factor (Kendall and Caldwell,
1998). This process may occur during biocalcification of
the shell of C. radula as (1) exchanges between the external
medium and the extravallial compartment are limited
(semi-closed system; see Wilbur and Saleuddin, 1983), lim-
iting the pool of HCO3− ions required by the reaction, and
(2) the product of this reaction (i.e., calcite) does not back-
react. If the effects of Rayleigh fractionation manifest
themselves in the oxygen isotope system, they will result in
18O enrichment in both the HCO3− reservoir and the
precipitated calcite, as previously suggested by Mickler
et al. (2004) to explain the offset from equilibrium they ob-
served in modern tropical speleothems.

4.3. Conclusions

This study highlights the potential use of shells as high
resolution archives of seawater temperature in New Cale-
donia. Our new δ18O:temperature relationship permits the
reconstruction of seasonal SST variations within ±1.0 °C
over the temperature range 20–30 °C. Accuracy could be
improved with better knowledge of the timing of striae
formation and with salinity measurements at higher tem-
poral resolution. We suggest that an observed 0.73‰
offset between the C. radula δ18O:temperature relationship and
a recent equation describing isotopic equilibrium in
inorganic calcite grown in seawater may be caused by
(1) differences in solution pH between the scallop’s extra-
valial fluid and seawater, (2) an isotopic signature of the
EPF different from that of seawater, or (3) Rayleigh frac-
tionation in both the HCO3− reservoir and the calcite pre-
cipitated from it. These hypotheses remain to be
demonstrated following detailed chemical analyses of the
EPF.

In the past decade, several authors examined geochem-
ical records (δ18O, Sr/Ca, Mg/Ca, U/Ca) of SST variabil-
ity in corals from the tropical southwest Pacific Ocean
(e.g., Kilbourne et al. (2004) and references therein).
These long-lived organisms can be used to reconstruct
SST variations over several centuries. However, subannu-
al SST reconstructions using corals are problematic be-
cause of the absence of clear sub-annual growth bands
(Risk and Pearce, 1992). In most high resolution coral
studies (e.g., Meibom et al., 2004), a chronology is de-
veloped by assuming constant growth rates and measuring
distance along a transect, even though corals are known
to exhibit highly variable daily growth rates (Risk and
Pearce, 1992). In contrast, scallop shells can provide short
SST time series (on the order of a few years) with very
high temporal resolution (circa-daily), thus providing
accurate estimates of the full range of environmental con-
ditions that these organisms experience while growing.
Scallops are thus more likely to record high frequency,
extreme environmental events, at least as long as the stress
induced does not interfere with the scallop’s growth. This
characteristic is particularly useful for the investigation of
coral bleaching events. Möberg et al. (2005) pointed out
the need for multi-proxy approaches for accurate recon-
struction of past seawater temperature variations, by com-
bining long, low-frequency data sets (such as from corals)
with high-frequency information (e.g., from scallop shell
data). As a large edible species, ancient C. radula speci-
mens are abundant at archaeological sites (J.-C. Gal-
paud, personal communication), and ancient shells may
also be found by coring fossil reef or sand units. In this
context, corals and scallops may become complementary
tools for SST reconstructions in the tropical southwest
Pacific.

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