



## Assessing the reproducibility and reliability of estuarine bivalve shells (*Saxidomus giganteus*) for sea surface temperature reconstruction: Implications for paleoclimate studies

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### Abstract

Studies using oxygen isotopes ( $\delta^{18}\text{O}$ ) of mollusk shells to determine paleotemperature need to assume water  $\delta^{18}\text{O}$  values, which could severely influence calculated temperatures. We analyzed aragonitic shells of the Butter Clam, *Saxidomus giganteus* (DeShayes, 1839), to determine the reproducibility of the isotopic signal between individuals and to assess how precisely temperature could be calculated given known salinity and temperature. Furthermore, carbon isotopes are also investigated as an environmental proxy. The abundance of well-preserved *S. giganteus* shells in archeological and geological deposits in northwestern North America makes them a particularly suitable species for paleoclimate studies. Seasonally resolved stable oxygen isotope profiles in three *S. giganteus* shells collected from the same site in Puget Sound (Washington, USA) were well correlated ( $0.77 < R^2 < 0.87$ ). Although there were differences up to 0.58‰ in high resolution  $\delta^{18}\text{O}$  profiles of the three shells, the difference between the average  $\delta^{18}\text{O}$  of each shell was less than half of this (0.19‰) and half of what has been reported for between-colony coral variability.  $\delta^{13}\text{C}$  profiles on the other hand were more complex, with shell  $\delta^{13}\text{C}$  being about 2.5‰ lower than expected equilibrium values. However, this roughly conforms to the idea that about 10% of the shell carbon originates from metabolic  $\text{CO}_2$ . Both  $\delta^{18}\text{O}$  and  $\delta^{13}\text{C}$  indicate that *S. giganteus* do not grow during periods of reduced salinity. Despite the excellent reproducibility of  $\delta^{18}\text{O}$  between shells, and the fact that salinity effects were duly considered, calculated temperature still differed from instrumental temperature. Applying different salinity– $\delta^{18}\text{O}$  water relationships to average shell  $\delta^{18}\text{O}$ , and considering salinity from the shell collection site and a nearby offshore station resulted in calculated average water temperatures ranging from 1.7 to 6.4 °C warmer than measured. Although we could not determine if *S. giganteus* precipitate their shells in isotopic equilibrium, we believe that the difficulty in predicting temperature arose from not being able to accurately determine

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$\delta^{18}\text{O}$  of the water at the time of shell precipitation. These data highlight the difficulties inherent to using stable isotope profiles of estuarine biogenic carbonates as environmental proxies.

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## 1. Introduction

Ever since the pioneering work of Epstein et al. (1953) it has been well known that the oxygen isotopic signature recorded in mollusk shells ( $\delta^{18}\text{O}_\text{S}$ ) not only reflects the temperature during crystallization, but also the oxygen isotopic ratio of the water ( $\delta^{18}\text{O}_\text{W}$ ) within which they formed. Despite this, many studies have utilized  $\delta^{18}\text{O}_\text{S}$  as a temperature proxy using assumed  $\delta^{18}\text{O}_\text{W}$  (e.g., Weidman et al., 1994; Purton and Brasier, 1997). Carbon isotopes in biogenic carbonates, on the other hand, were originally hoped to record the isotopic signature of seawater dissolved inorganic carbon (DIC) (e.g., Mook and Vogel, 1968), which can provide information about salinity, anthropogenic carbon inputs and productivity. However, more recent work has shown the complications with this proxy due to the incorporation of metabolic  $\text{CO}_2$  (e.g., McConnaughey 1989; McConnaughey et al., 1997; Lorrain et al., 2004).

Bivalves are beneficial in that they can provide seasonal records of environmental conditions and have a wide geographic distribution, whereas many other proxies, such as corals, are limited in their latitudinal extent. Previous workers have used isotope ratios in bivalve shells as both salinity (e.g., Ingram et al., 1996) and temperature proxies (e.g., Weidman et al., 1994; Surge et al., 2001). Many paleoclimatic studies (e.g., Purton and Brasier, 1997; Dutton et al., 2002; Holmden and Hudson, 2003) rely on the assumption that bivalves fractionate isotopes in accordance with the well-established empirically determined paleotemperature equations for biogenic carbonates (e.g., Epstein et al., 1953; Grossman and Ku, 1986; Böhm et al., 2000). However, without species-specific verification with recent specimens, this is a risky practice. As opposed to corals and brachiopods, bivalves do generally secrete their skeletons in equilibrium (cf. Wefer and Berger, 1991), yet this might not always hold true (e.g., Owen et al., 2002). In addition, bivalve physiology also plays an

important role in the stable isotope ratios recorded in the shells due to the effect of temperature and salinity on growth. Bivalves may be euryhaline or stenohaline and may continue to grow in extreme temperatures or have minimum and or maximum temperature growth hiatuses, all of which will affect the isotopic signal recorded in the shell. The effect of rapidly changing temperature and salinity is especially important in coastal areas and even more so in estuaries.

Coastal settings were important to early people, resulting in numerous shell middens spanning the late Quaternary (e.g., Hetherington and Reid, 2003). It would be beneficial to both archeologists and paleoclimatologists to have well calibrated proxies of temperature in these regions. However, the fact that these regions can be highly dynamic in nature and the stable isotope ratios in carbonates are dependent on the isotope ratio of the water, which co-varies with salinity, make many of these areas difficult for isotope geochemistry.

This study aims to determine the reproducibility of the isotopic signal between individuals and to assess how precisely temperature can be calculated from *Saxidomus giganteus* (DeShayes, 1839)  $\delta^{18}\text{O}_\text{S}$ , given known instrumental temperature and salinity. Furthermore, the carbon isotope chemistry is investigated as a proxy of the carbon isotopic signature of DIC ( $\delta^{13}\text{C}_\text{DIC}$ ). The Butter clam, *S. giganteus*, is an aragonitic infaunal marine clam usually inhabiting the intertidal zone, but which can occur at depths in excess of 30 m (Quayle and Bourne, 1972). They are a temperate species, which cannot survive in very cold waters or reduced salinities (Bernard, 1983; Hetherington and Reid, 2003). *S. giganteus* has been continuously present as far north as British Columbia for the past ~12,000 years and probably was an important food source for early peoples as early as 9,000 years BP (Hetherington and Reid, 2003), and continue to be harvested today (Quayle and Bourne, 1972). *S. giganteus* are commonly found in prehistoric midden sites (Hetherington and Reid,

2003; Taylor, 2004) as well as in Pleistocene geologic deposits as well-preserved fossils (Kvenvolden et al., 1979), potentially making them a very useful paleo-environmental proxy.

To determine the reliability of *S. giganteus* as a recorder of environmental conditions, we analyzed three specimens that grew in the same area under the premise that if the isotope chemistry of the shells reflects an external environmental forcing, the signal should be similar in each shell. We then compare our results with environmental parameters to ascertain the accuracy and potential problems of using estuarine bivalves as paleo-environmental proxies.

## 2. Materials and methods

Three specimens of *S. giganteus* were collected alive from the same area (within ~10 m) in Puget Sound, near Carkeek Park, North Seattle, WA, USA

(N47°42'45" W122°22'46") on 18 September 2001 (Fig. 1). They were collected in gravely mud about 30 cm above mean spring low tide. The shells were carefully opened with a knife and were air-dried after tissue was removed. Sections of the shells were cut with a diamond saw along the axis of maximal growth, rinsed with deionised water, air-dried and mounted on microscopic slides.

Each section cut from a valve represents a series of successive growth increments. The sections were mounted on a computer controlled Merchantek Micro-mill Sampler (a fixed drill and computer controlled micro positioning device), which allows precise sampling. High resolution profiles were obtained by milling a succession of adjacent grooves 600 µm in length, 200 µm depth and 300 µm width, using a 300 µm bit (325 µm deep spots were used near the umbo due to the thinning of the carbonate layer). Grooves were milled parallel to the growth increments, along a transect from the youngest material

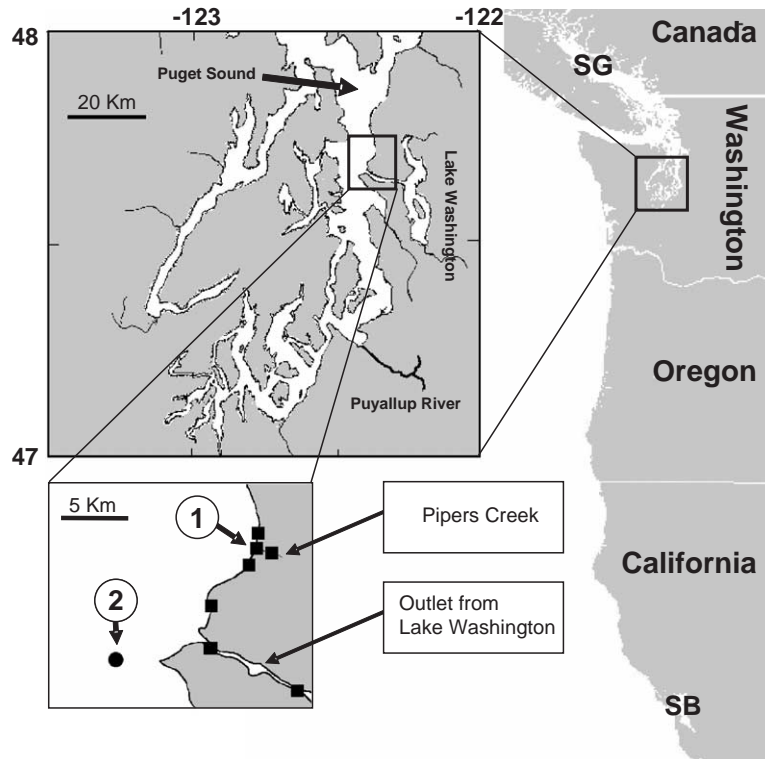


Fig. 1. Map of the West Coast of North America with detailed maps indicating the shell collection site (1) and the offshore station PSB003 (2) as well as water sampling sites (squares). The Puyallup River, Strait of Georgia (SG) and San Francisco Bay (SB) are also shown.

(growing tip) to the oldest (umbo) in the aragonite outer layer of the shell section (Fig. 2). Shells were not sampled completely to the umbo because the outer layer became too thin to sample; shell three was only partially sampled. We tested various drill speeds, as well as manual sampling (scraping with scalpel blade), to see if heating during drilling could have caused mineralogical transformation into calcite (cf. Gill et al., 1995), however, no significant differences were noted in isotope ratios. Additional samples (9 per shell) were collected from the inner layer near the umbo (Fig. 2), which should integrate the isotopic signal over the entire life of the animal.

All isotope analyses were carried out in the Stable Isotope Laboratory of the Vrije Universiteit Brussel, Belgium. Shell oxygen ( $\delta^{18}\text{O}_\text{S}$ ) and carbon ( $\delta^{13}\text{C}_\text{S}$ ) isotope analysis were performed using a ThermoFinnigan Kiel III (an automated carbonate preparation device) coupled to a ThermoFinnigan Delta+XL dual inlet isotope ratio mass spectrometer (IRMS). Using anhydrous phosphoric acid, the carbonate of the sample is transformed into  $\text{CO}_2$ , which is cryogenically purified with liquid nitrogen. The samples were calibrated against the standard NBS-19 ( $\delta^{18}\text{O} = -2.20\text{‰}$ ,  $\delta^{13}\text{C} = +1.95\text{‰}$ ) and data are reported as ‰ VPDB using the conventional delta notation:

$$\delta^{18}\text{O} \text{ or } \delta^{13}\text{C} = (R_{\text{sample}}/R_{\text{standard}} - 1) * 1000 \quad (1)$$

with  $R = {}^{18}\text{O}/{}^{16}\text{O}$  or  ${}^{13}\text{C}/{}^{12}\text{C}$ . The reproducibility ( $1\sigma$ ) of the routinely analyzed carbonate standard (NBS-19) was  $0.08\text{‰}$  for  $\delta^{18}\text{O}$  and  $0.04\text{‰}$  for  $\delta^{13}\text{C}$  ( $n=286$ ). Furthermore, the lighter standard, NBS-18 ( $\delta^{18}\text{O} = -23.05\text{‰}$ ,  $\delta^{13}\text{C} = -5.04\text{‰}$ ), gave similar precision and was within  $0.01\text{‰}$  of the recommended values ( $n=22$ ).

As no data on Puget Sound water oxygen isotope chemistry could be found in the literature, nearshore water samples were collected on 29 May 2003 for determination of salinity,  $\delta^{18}\text{O}$  and  $\delta^{13}\text{C}_\text{DIC}$  from the

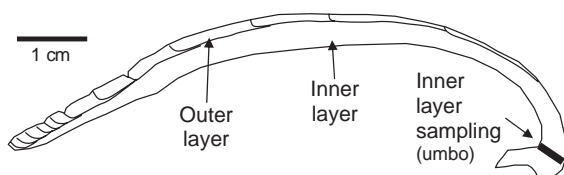


Fig. 2. Cross section of *Saxidomus giganteus* shell showing the successive growth increments in the outer layer of the shell.

outlet from Lake Washington (Salmon Bay; freshwater) to about 800 m north of Carkeek Park, including Pipers Creek, the small freshwater stream draining into the shell collection area (Fig. 1).  $\delta^{18}\text{O}_\text{W}$  was determined by the conventional  $\text{CO}_2\text{--H}_2\text{O}$  equilibration method, similar to Prosser et al. (1991). Precision was better than  $0.15\text{‰}$  ( $1\sigma$ ) by analysis of seawater standards calibrated against VSMOW.  $\delta^{13}\text{C}_\text{DIC}$  was determined by acidifying 5 ml of water in an 8 ml helium flushed headspace vial and subsequently injecting 400  $\mu\text{l}$  of the headspace into the carrier gas stream of a ThermoFinnigan Delta+XL continuous flow IRMS.  $\delta^{13}\text{C}_\text{DIC}$  precision was better than  $0.2\text{‰}$  based on replicate measurements; data were corrected using calibrated  $\text{CO}_2$  gas according to Miyajima et al. (1995) and are given vs. VPDB. Salinity was estimated from  $\text{Na}^+$  concentrations (measured by ICP-OES) using the equation:

$$\text{Salinity} = \mu\text{g g}^{-1} \text{Na}^+ * 35 / 10783.7 \quad (2)$$

considering  $10783.7 \mu\text{g g}^{-1} \text{Na}^+$  at a salinity of 35 (DOE, 1994); with an analytical precision of  $\pm 0.25$  salinity units.

Monthly measurements of nearshore temperature and salinity from Carkeek Park were obtained from the King County Environmental Laboratory. This data set is not complete and only extends to 1997, while  $\delta^{18}\text{O}_\text{S}$  data suggest these shells started growing in 1991 (see Results). To extend the data set we used data from an offshore station (station PSB003, situated at approximately 10 km from the sampling area; Fig. 1), monitored since 1971 (also monthly) by the Washington State Department of Ecology's Environmental Information Management System project (<http://www.ecy.wa.gov/eim>). The offshore station was sampled at a depth of 0.5 m, but overlies 110 m of water. Water temperature is well correlated between both stations ( $R^2=0.83$ ,  $p<0.0001$ ,  $n=36$ ; Fig. 3A) allowing us to construct a temperature record back to 1991. However, summer water temperatures are higher at the nearshore station (Carkeek). Salinity is not correlated ( $R^2=0.14$ ,  $p=0.062$ ,  $n=26$ ) and is generally less variable at the offshore station (Fig. 3B). Average monthly precipitation (1994–2001) for Seattle was obtained from the NOAA (2003) and shows that salinity drops are not always related to precipitation events (Fig. 3B).

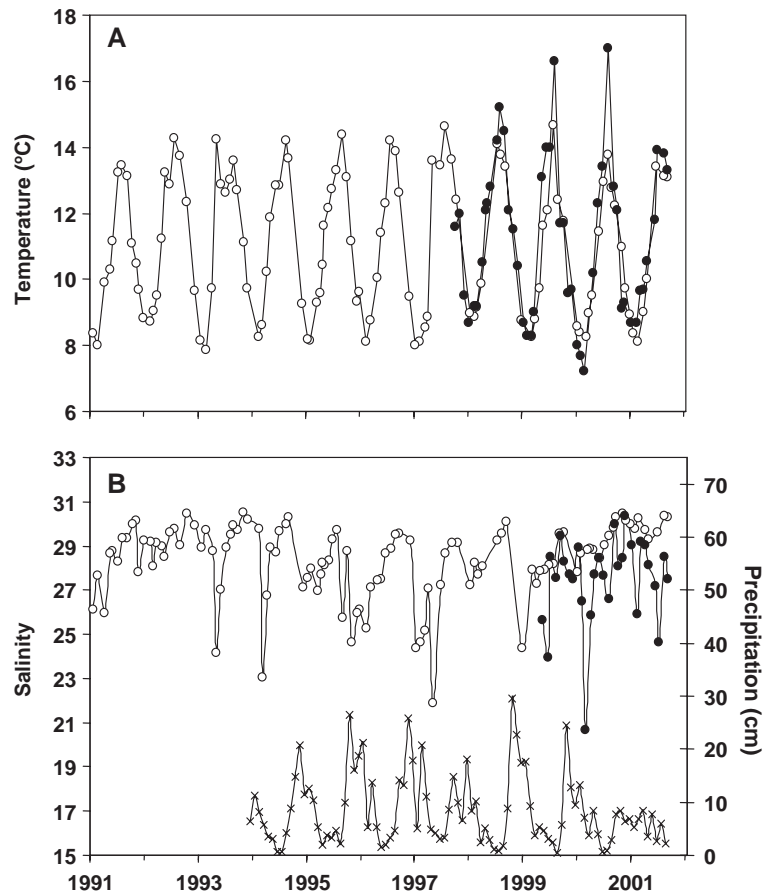


Fig. 3. (A) Temperature records at both the shell collection site (Carkeek Park; solid circles) and at the offshore station (PSB003; open circles) and (B) salinity data from both stations (symbols as in A) as well as monthly average precipitation data from Seattle, Washington (crosses).

The aragonite paleotemperature equation of Böhm et al. (2000) was used to estimate temperature from  $\delta^{18}\text{O}_S$ :

$$T(^{\circ}\text{C}) = (20.0 \pm 0.2) - (4.42 \pm 0.10) * (\delta^{18}\text{O}_S - \delta^{18}\text{O}_W); \text{ for } 3^{\circ} < T < 28^{\circ} \quad (3)$$

which is largely based on the equation of Grossman and Ku (1986) and includes many taxa of aragonite precipitating organisms.

### 3. Results

When both  $\delta^{13}\text{C}_{\text{DIC}}$  and  $\delta^{18}\text{O}_W$  are plotted against salinity, the water samples from the outlet of Lake

Washington are clearly not following the same mixing lines as the water samples taken nearby the shell collection site (Fig. 4). Excluding the two samples from the outlet of Lake Washington, there are excellent linear relationships between salinity and isotopes, with  $\delta^{18}\text{O}_W = 0.309 * \text{Salinity} - 10.49$  ( $R^2 = 0.998$ ,  $p < 0.0001$ ,  $n = 5$ ) and  $\delta^{13}\text{C}_{\text{DIC}} = 0.573 * \text{Salinity} - 16.54$  ( $R^2 = 0.997$ ,  $p < 0.0001$ ,  $n = 5$ ).

Profiles of  $\delta^{18}\text{O}_S$  and  $\delta^{13}\text{C}_S$  are plotted against sampling distance from the umbo (oldest carbonate) (Fig. 5). Each shell exhibits a clear seasonal pattern in  $\delta^{18}\text{O}_S$ , with the most negative values representing the warmest summer water temperatures.  $\delta^{13}\text{C}_S$  tends to follow a trend of the most negative values falling in the spring or summer (less so in shell 3) (Fig. 5). Averages and ranges of isotope data, as well as results

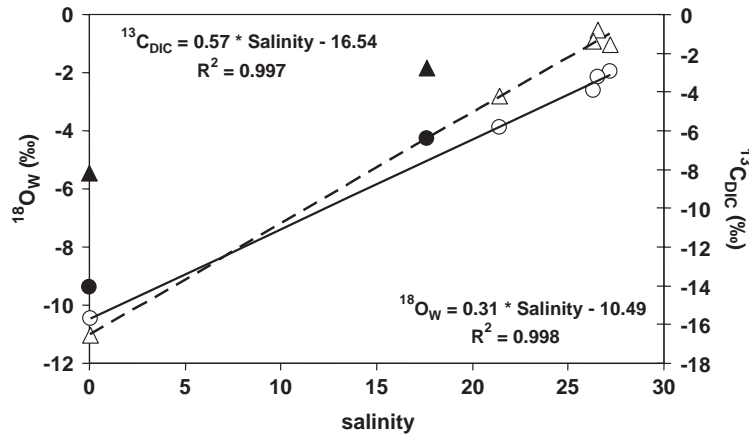


Fig. 4. Regressions of  $\delta^{18}\text{O}_W$  (circles, solid line) and  $\delta^{13}\text{C}_{\text{DIC}}$  (triangles, dashed line) vs. salinity from nearby the collection site (collected on 29 May 2003). Data from the water samples collected from the outlet of Lake Washington were not included in the regression and are shown as solid symbols.

from the inner layer sampling, can be found in Table 1. The average high resolution  $\delta^{18}\text{O}_S$  values were in good agreement between shells, with a maximum difference of 0.19‰. Furthermore, the inner layer  $\delta^{18}\text{O}_S$  represented the average shell well, with a maximum difference of 0.24‰. High resolution  $\delta^{13}\text{C}_S$  on the other hand was variable between the three shells,

but was within the same 2‰ range for all shells (Fig. 5). Average high resolution  $\delta^{13}\text{C}_S$  values were within 0.37‰ for the three shells and was similar to differences in the inner layer (maximum difference of 0.41‰; Table 1).  $\delta^{13}\text{C}_S$  and  $\delta^{18}\text{O}_S$  exhibit a very weak positive correlation in shells 1 ( $R^2=0.05$ ,  $p<0.01$ ,  $n=190$ ) and 2 ( $R^2=0.19$ ,  $p<0.0001$ ,

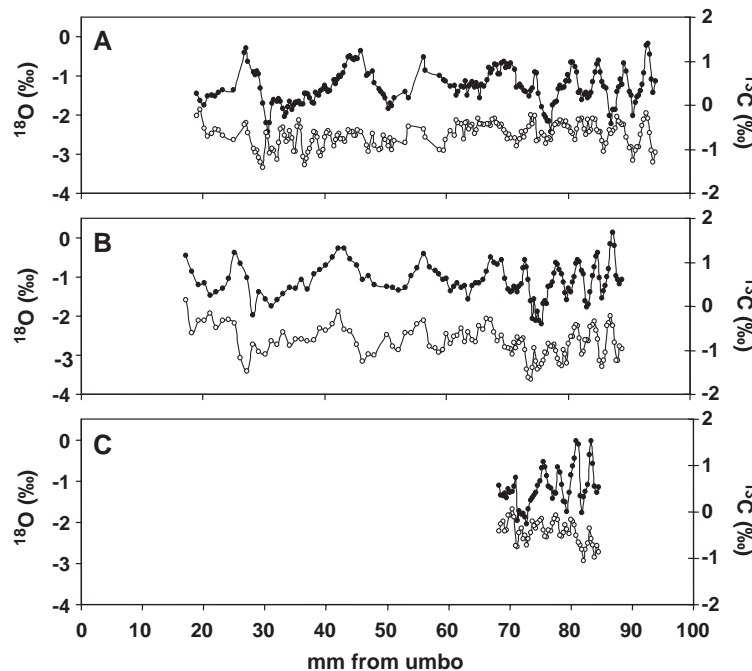


Fig. 5. Plots of  $\delta^{18}\text{O}_S$  (solid circles) and  $\delta^{13}\text{C}_S$  (open circles) vs. distance from the umbo for the three clams (A: shell 1, B: shell 2, C: shell 3).

Table 1

Average, standard deviation, and minimum and maximum  $\delta^{18}\text{O}_\text{S}$  and  $\delta^{13}\text{C}_\text{S}$  from the three shells as well as the average values obtained from the inner layer near the umbo (see Fig. 2)

	Shell 1	Shell 2	Shell 3
Average $\delta^{18}\text{O}_\text{S}$	$-1.29 \pm 0.44$	$-1.10 \pm 0.44$	$-1.16 \pm 0.47$
Minimum $\delta^{18}\text{O}_\text{S}$	-2.44	-2.21	-2.04
Maximum $\delta^{18}\text{O}_\text{S}$	-0.18	0.13	-0.03
Inner layer $\delta^{18}\text{O}_\text{S}$	$-1.08 \pm 0.09$	$-1.34 \pm 0.08$	$-1.23 \pm 0.15$
Average $\delta^{13}\text{C}_\text{S}$	$-0.67 \pm 0.26$	$-0.81 \pm 0.34$	$-0.44 \pm 0.25$
Minimum $\delta^{13}\text{C}_\text{S}$	-1.41	-1.66	-1.06
Maximum $\delta^{13}\text{C}_\text{S}$	-0.10	0.15	0.06
Inner layer $\delta^{13}\text{C}_\text{S}$	$-0.72 \pm 0.15$	$-1.04 \pm 0.29$	$-0.85 \pm 0.18$
$n^a$	190	123	55

All data in ‰;  $n$  = number of samples.

<sup>a</sup> Inner layer samples are an average of 9 samples.

$n = 123$ ) but not in shell 3 ( $R^2 = 0.01$ ,  $p = 0.54$ ,  $n = 55$ ). Growth rates show a strong decrease through ontogeny, typical of bivalves; although the trend is similar for all shells, there are differences of more than 4 mm  $\text{yr}^{-1}$  (i.e., 1994) between shells (Fig. 6).

To test the reproducibility of the signal recorded in *S. giganteus* shells, the data first need to be fit on the same time axis to correct for differences in growth rate.  $\delta^{18}\text{O}_\text{S}$  profiles from shells 1 and 3 were fit to the  $x$ -axis of shell 2 (shell 2 arbitrarily chosen) using a phase demodulation method (Fig. 7; see De Ridder et al., 2004). Briefly, this method is based on the periodicity of the signal and uses the side peaks in the Fourier spectrum to model the variations in growth.

Once the growth is known, the time axis ( $x$ -axis) can be scaled accordingly. Using this method, there is excellent agreement between the three profiles (shell 1 vs. 2,  $R^2 = 0.87$ ; 1 vs. 3,  $R^2 = 0.81$ ; 2 vs. 3,  $R^2 = 0.77$ ;  $p < 0.0001$  for all; Fig. 7).

## 4. Discussion

### 4.1. Reproducibility

Despite the excellent  $\delta^{18}\text{O}_\text{S}$  correlations between the three shells, there are still important differences of up to 0.58‰ (Fig. 7). The offset could be a result of either real differences in  $\delta^{18}\text{O}_\text{S}$  or may be the result of time averaging caused by differences in growth rate between shells. Time averaging occurs when shell growth slows and sample interval (i.e., drill spacing) remains the same, resulting in the same sample size representing (and averaging) more time. Time averaging will thus bring the amplitude of the  $\delta^{18}\text{O}_\text{S}$  cycle closer to the mean (see Goodwin et al., 2003). Indeed, for the years with the largest  $\delta^{18}\text{O}_\text{S}$  differences (see Fig. 7), the shells exhibit large differences in growth rates (Fig. 6). For example, in the last three years of growth, shell 1 grew 1.4 to 2 times faster than shell 3. This could help explain the reduced summer  $\delta^{18}\text{O}_\text{S}$  values in shell 3, but not the winter difference where shell 3 has the larger amplitude. Furthermore, these differences may be caused by physiological differ-

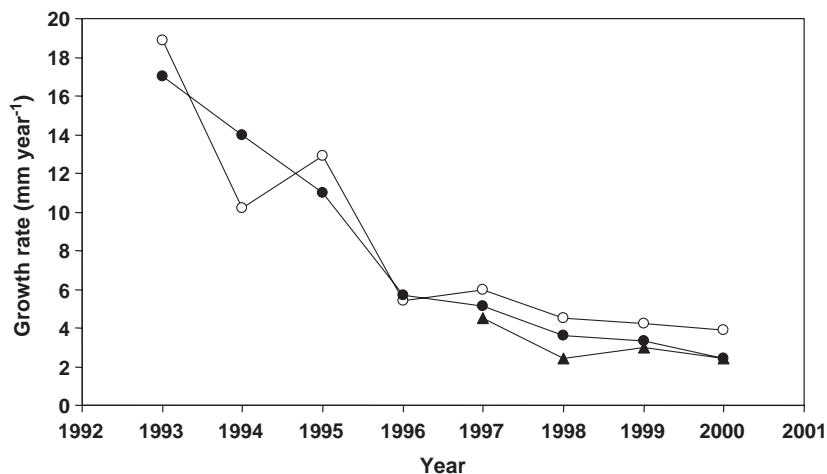


Fig. 6. Annual growth rates calculated from the distance along the shell between  $\delta^{18}\text{O}_\text{S}$  maxima (shell 1: open circles, shell 2: solid circles, shell 3: triangles).

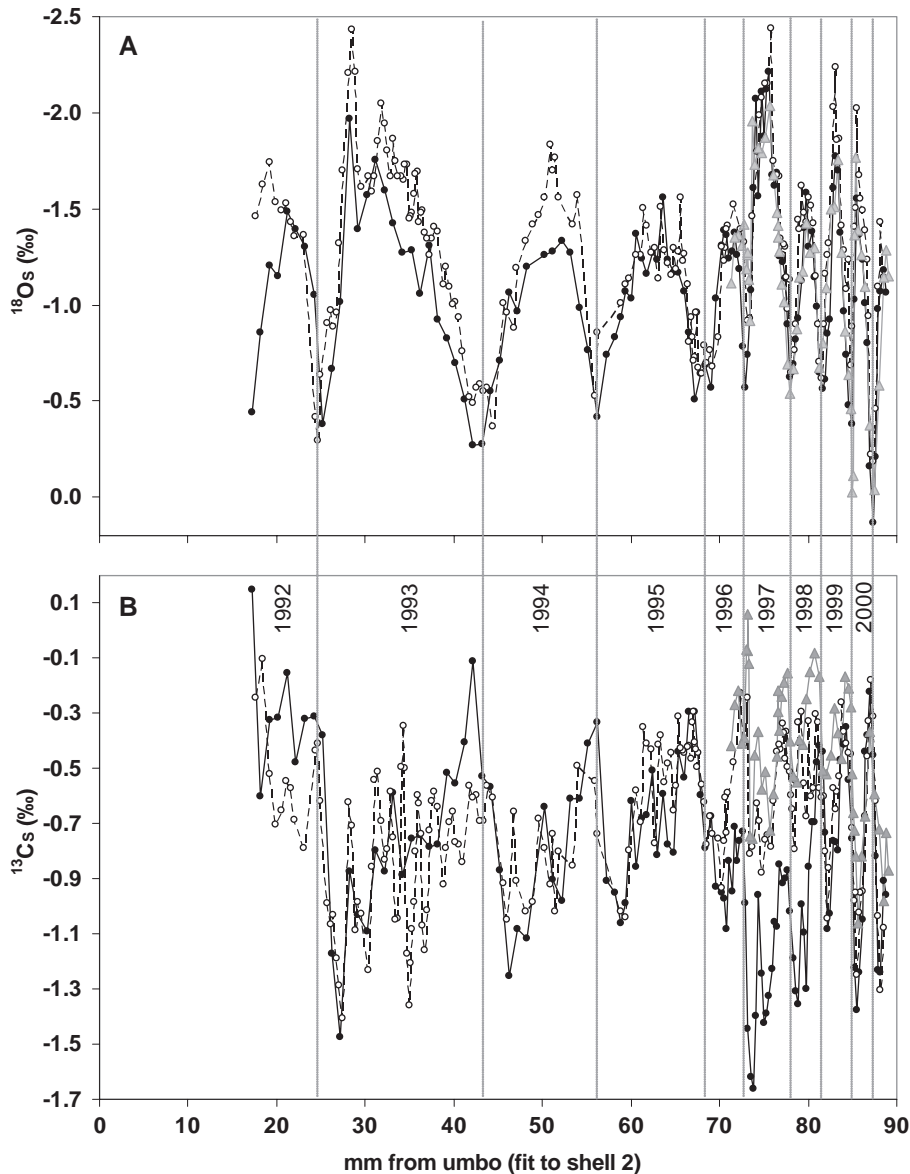


Fig. 7.  $\delta^{18}\text{O}_s$  (A; y-axis inverted) and  $\delta^{13}\text{C}_s$  (B) of the three shells fit to the x-axis of shell 2 (shell 1: open circles, shell 2: solid circles, shell 3: triangles). Growth years are approximated by dotted lines.

ences between clams, with some clams precipitating their shells during certain hours of the day (e.g., cool mornings; cf. Goodwin et al., 2001). Finally, they might be the result of micro-site conditions being different where the individual clams grew, e.g., groundwater outflow can be limited to very small patches in the intertidal zone (e.g., Kohout and Koli-pinski, 1967). Whether or not these differences reflect

real environmental differences, or are the result of vital effects cannot be determined here. The maximum difference between the shells ( $\sim 0.5\text{‰}$ ) results in a maximum calculated temperature difference of about  $2.2\text{ }^\circ\text{C}$ . Elliot et al. (2003) found similar differences between *Mercenaria mercenaria* (Linnaeus, 1758) shells grown at the same locale, which they attributed to variation in growth rates between the shells (i.e., an



averaging effect). This illustrates the bias that can be expected when working on only one shell. However, it should be noted that the differences between the average  $\delta^{18}\text{O}_\text{S}$  were smaller (Table 1; the maximum difference is 0.19‰ between shell 1 and 2) and about half of that recorded in between-colony coral variability (0.4‰; Linsley et al., 1999). This suggests that the difference in average calculated temperatures based on different shells in this population is on the order of 0.8 °C.

All  $\delta^{13}\text{C}_\text{S}$  data were within the same 1.9‰ range, however were not well correlated overall. It is interesting to note that in the high resolution profiles of  $\delta^{13}\text{C}_\text{S}$ , all three shells synchronize during the last two years measured, and shells 1 and 2 show some correlation in the first four years (Fig. 7). However, we were unable to find an adequate explanation why in some years they synchronize (e.g., 1994–1995, 2000–2001) and in others they don't.

The similarities between the  $\delta^{18}\text{O}_\text{S}$  averages of the high resolution sampling of the outer layer and the  $\delta^{18}\text{O}_\text{S}$  data from the inner layer (Table 1) confirm that the inner layer may be used to obtain a fast and inexpensive average  $\delta^{18}\text{O}_\text{S}$ .  $\delta^{13}\text{C}_\text{S}$  was also similar between the two methods for shells 1 and 2, but was on average 0.41‰ more negative than the high resolution outer layer average of shell 3, which could be an effect of  $\delta^{13}\text{C}_\text{S}$  becoming more positive through ontogeny as was observed in shell 1.

#### 4.2. Oxygen isotopes

When daily growth increments are present, they can easily be used to date the incremental samples (e.g., Schöne et al., 2003; Lorrain et al., 2004). However, when daily increments are not easily discernible, the usual method used to assign a time scale to the  $\delta^{18}\text{O}_\text{S}$  record is to compare measured and predicted

$\delta^{18}\text{O}_\text{S}$  (e.g., Klein et al., 1996a,b; Auclair et al., 2003; Elliot et al., 2003). Predicted  $\delta^{18}\text{O}_\text{S}$  is calculated using a paleotemperature equation (e.g., Böhm et al., 2000), where instrumental temperature is known and  $\delta^{18}\text{O}_\text{W}$  usually is calculated from its relationship with salinity.

Understanding the salinity– $\delta^{18}\text{O}_\text{W}$  relationship is crucial when calculating temperature from  $\delta^{18}\text{O}_\text{S}$ , especially in estuarine conditions. For example, only a 0.25‰ change in  $\delta^{18}\text{O}_\text{W}$  (or roughly about 1 PSU at our site) results in a 1.1 °C temperature difference. We acknowledge the shortcomings of collecting  $\delta^{18}\text{O}_\text{W}$  data from only one day as  $\delta^{18}\text{O}_\text{W}$  may change seasonally due to changes in the  $\delta^{18}\text{O}$  of precipitation (and glacial melt water volume). However, we could not find any published data available from Puget Sound regarding  $\delta^{18}\text{O}_\text{W}$ . Carpenter and Lohmann (1995) mistakenly reported the data of Klein et al. (1996b) were from Puget Sound, but they were actually taken 200 km to the north at the northern end of the Strait of Georgia, British Columbia, Canada (see Fig. 1 for location; Klein et al., 1996b). Auclair et al. (2003), working on brachiopods from Puget Sound, used a simple mass balance equation based on theoretical marine water (34.5 PSU=0‰) and freshwater (0 PSU=−14‰) endmembers. Due to the fact that we cannot be certain about our salinity– $\delta^{18}\text{O}_\text{W}$  relationship, we explored other published data from the region. Five regression equations were tested (see Table 2): 1) Klein et al. (1996b) from the Strait of Georgia, 2) Ingram et al. (1996) from San Francisco Bay, 3) our data, 4) Auclair et al. (2003; see above), and 5) a mixing model based on the freshwater endmember of Coplen and Kendall (2000;  $\delta^{18}\text{O}_\text{W}$  from the Puyallup River, which flows into southern Puget Sound (Fig. 1), measured on several occasions between 1984 and 1987 ( $\delta^{18}\text{O}_\text{W}$  =  $-12.4 \pm 1.3\text{‰}$ )) and the marine endmember of Epstein and Mayeda (1953;  $\delta^{18}\text{O}_\text{W}$  of ocean surface water sampled along the Northwest

Table 2  
West Coast  $\delta^{18}\text{O}_\text{W}$ –salinity relationships from various studies ( $\delta^{18}\text{O}_\text{W}$ =Salinity\*b+a)

Location	Relation to study site	Slope (b)	Intercept (a)	Reference
Strait of Georgia	± 200 km north	0.39	−13.50	Klein et al. (1996b)
Puget Sound	Near collection site	0.31	−10.49	This study
Puget Sound	Theoretical	0.41	−14.00	Auclair et al. (2003)
Puget Sound+Pacific	Nearby collection site (see text)	0.36	−12.44	Epstein and Mayeda (1953) and Coplen and Kendall (2000)
San Francisco Bay	± 1300 km south	0.32	−10.95	Ingram et al. (1996)

coast ( $32.6 \pm 0.3$  PSU;  $\delta^{18}\text{O}_W = -0.95 \pm 0.18\text{‰}$ ) (hereafter referred to as EM and CK). Using these salinity– $\delta^{18}\text{O}_W$  relationships results in a maximum average predicted carbonate difference of  $0.77\text{‰}$  (or  $3.4\text{ °C}$ ) when using the equation of Böhm et al. (2000) (equations are summarized in Table 2 and sampling sites are shown in Fig. 1). The largest difference is between our data and the data of Klein et al. (1996b). However, the use of our salinity– $\delta^{18}\text{O}_W$  relationship is not necessarily the best choice. The data of Ingram et al. (1996; San Francisco Bay) and Klein et al. (1996b; Strait of Georgia) were both taken during a full year and bracket our sampling site to the South and North, respectively (see Fig. 1). When considering that  $\delta^{18}\text{O}$  of precipitation becomes more negative northward along the west coast of North America (IAEA, 2001; Coplen and Kendall, 2000), it is also expected that slopes between salinity and  $\delta^{18}\text{O}_W$  become larger and intercepts more negative toward the north. Theoretically, the slope and intercept of the salinity– $\delta^{18}\text{O}_W$  relationship at our site should fall between these two equations. Neither our data, nor the relationship of Auclair et al. (2003) are bracketed by these equations, whereas the EM and CK equation is (Table 2). This could point to the fact that the Auclair et al. (2003) equation and our equation are not appropriate for

Puget Sound. However, when taking a closer look at the predictability of these equations in the salinity range of interest ( $\sim 20\text{--}30$  PSU), the 95% prediction intervals from Klein et al. (1996b) and Ingram et al. (1996) greatly overlap (Fig. 8). This is most likely caused by the large seasonal fluctuations in  $\delta^{18}\text{O}$  of precipitation and river run-off (IAEA, 2001; Coplen and Kendall, 2000). We therefore consider our  $\delta^{18}\text{O}_W$  as unknown due to the poor predictability of these equations.

Considering that we do not have a well constrained salinity– $\delta^{18}\text{O}_W$  relationship we cannot calculate a reliable predicted  $\delta^{18}\text{O}_S$ . Furthermore, we cannot solve Eq. (3) for  $\delta^{18}\text{O}_W$  being that we do not have a temperature for each  $\delta^{18}\text{O}_S$ . Therefore our only option is to calculate temperature from  $\delta^{18}\text{O}_S$ , using a constant  $\delta^{18}\text{O}_W$ , and to compare this with the instrumental temperature record. We calculated that the average modeled temperature best matched the average instrumental temperature ( $11.4\text{ °C}$ ) when using a  $\delta^{18}\text{O}_W$  of  $-3.12\text{‰}$ . To reduce the bias of any one shell, we calculated an average  $\delta^{18}\text{O}_S$  profile from the three shells, using a phase demodulation method (De Ridder et al., 2004), and fit our modeled temperature record to the instrumental temperature record using the same technique. This procedure resulted in a

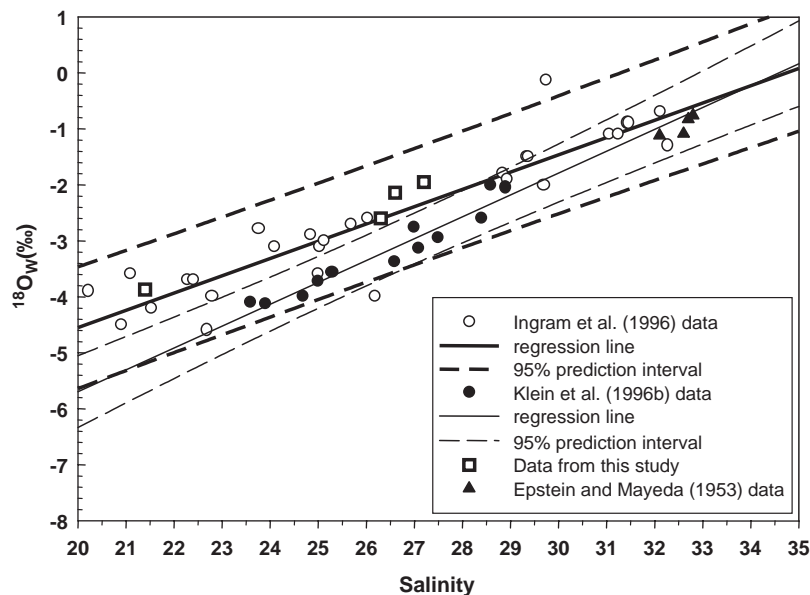


Fig. 8. Regressions and 95% prediction intervals of salinity and  $\delta^{18}\text{O}_W$  for the salinity range of interest. Data from San Francisco Bay (Ingram et al., 1996) and the Strait of Georgia, B.C. (Klein et al., 1996b). Data from Epstein and Mayeda (1953) and data from this study are also plotted.

reasonable fit with a correlation ( $R^2$ ) of 83% ( $p < 0.001$ ; Fig. 9). As there is a good fit between both minima and maxima of many years, *S. giganteus* does not seem to have a growth shut down temperature (temperature where they stop growing) in this temperature range. However, the extreme summer temperatures recorded at Carkeek (which are monthly point measurements) were not recorded in the shell. This could either be the result of *S. giganteus* not precipitating during the warmest summer days or that these warm temperatures last a short time and are averaged with cooler temperatures when sampling the shell. As Bernard (1983) reported that the upper thermal threshold of *S. giganteus* is above 20 °C, and the warmest temperatures here are about 18 °C, the latter seems more likely, but only daily water temperature data could give a definitive answer.

The calculated  $\delta^{18}\text{O}_\text{W}$  which fit best with our data ( $-3.12\text{‰}$ ) corresponds to a salinity range of about 21–28 (considering the 95% prediction intervals, Fig. 8), which is the lower range of salinities observed at our site ( $27.5 \pm 2.0$ ; Fig. 3) and 0.5‰ more negative than the average  $\delta^{18}\text{O}_\text{W}$  calculated using the EM and KC equation ( $-2.52 \pm 0.72\text{‰}$ ). This could imply that these bivalves are precipitating out of equilibrium. There are several factors that could cause disequilib-

rium. Mineralogy is important as calcite is depleted in  $^{18}\text{O}$  by about 0.6‰ relative to aragonite (Tarutani et al., 1969), however *S. giganteus* shells are composed almost entirely of aragonite based on XRD analysis and minor element composition (Ulens, 2003; Gillikin et al., 2005). Kinetic effects can cause depletions in  $^{18}\text{O}$  relative to equilibrium when  $\text{CaCO}_3$  precipitation is fast enough to allow precipitation of  $\text{HCO}_3^-$  and  $\text{CO}_3^{2-}$  before equilibration with  $\text{H}_2\text{O}$  (McConnaughey, 1989). However, kinetic effects usually act on both carbon and oxygen isotopes; considering the fact that  $\delta^{18}\text{O}_\text{S}$  and  $\delta^{13}\text{C}_\text{S}$  were poorly correlated in all shells, kinetic effects most likely are very small (McConnaughey, 1989). pH differences at the site of calcification can also cause deviations from equilibrium as was noted in both foraminifera (Spero et al., 1997) and corals (Rollion-Bard et al., 2003). Although we do not have data on the pH of *S. giganteus* extrapallial fluid (EPF, where calcification occurs), there is nothing in the limited data available on this animal's physiology (Bernard, 1983) that would suggest it to be greatly different from other aragonitic venerids, which do precipitate their shells in equilibrium (e.g., Weidman et al., 1994; Elliot et al., 2003). An alternative hypothesis is that the clams, which live buried in the sediment up to 30 cm deep (Qualye and Bourne,

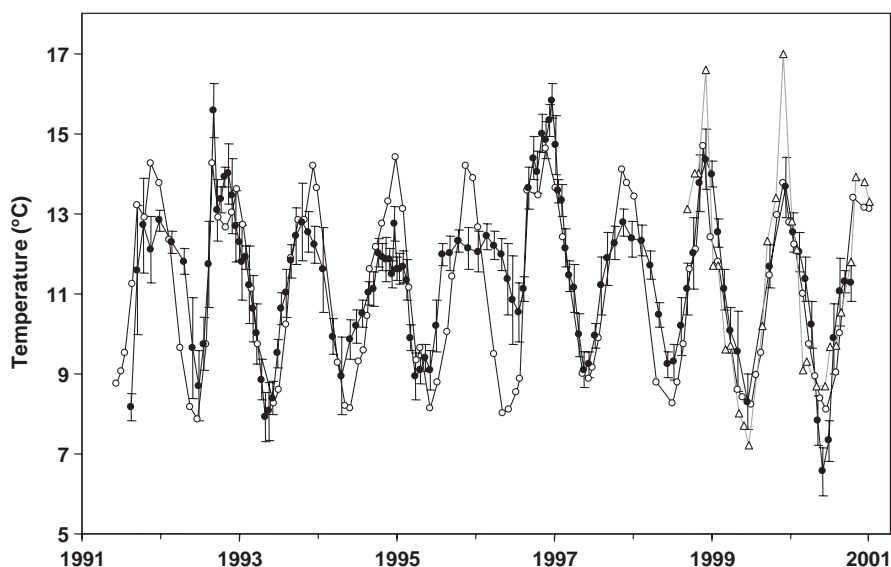


Fig. 9. Instrumental temperature from both the offshore station (PSB003; open circles) and the shell collection site (Carkeek Park; triangles) and the modeled temperature obtained from the average  $\delta^{18}\text{O}_\text{S}$  of the three shells (solid circles) using a constant  $\delta^{18}\text{O}_\text{W}$  of  $-3.12\text{‰}$  and the paleotemperature equation of Böhm et al. (2000); with standard error bars shown.

Table 3

Difference between average instrumental temperature and average modeled temperature ( $^{\circ}\text{C}$ ; calculated using the equation of Böhm et al., 2000) using data from the nearshore collection site (Carkeek, 1999–2001,  $n=22$ ) and the offshore station (PSB, 1992–2001,  $n=80$ ) for each salinity– $\delta^{18}\text{O}_\text{W}$  relationship (see text for details)

Salinity– $\delta^{18}\text{O}_\text{W}$ relationship	$\Delta T_{\text{Böhm PSB salinity}}$	$\Delta T_{\text{Böhm Carkeek salinity}}$
Klein et al. (1996b)	–3.0	–1.7
Ingram et al. (1996)	–5.6	–4.4
This study	–6.4	–5.2
Auclair et al. (2003)	–3.3	–1.9
EM and CK	–4.0	–2.7

EM and CK is the equation derived from the data of Epstein and Mayeda (1953) and Coplen and Kendall (2000).

1972), were affected by groundwater incursions (cf. Elliot et al., 2003). Groundwater can be expected to be depleted in  $^{18}\text{O}$  as well as to reduce salinity, therefore making the source  $\delta^{18}\text{O}_\text{W}$  more negative.

Often studies employ salinity– $\delta^{18}\text{O}_\text{W}$  relationships from nearby areas, use theoretical endmembers to relate salinity to  $\delta^{18}\text{O}_\text{W}$ , or assume a constant  $\delta^{18}\text{O}_\text{W}$  (e.g., Weidman et al., 1994; Goodwin et al., 2001; Auclair et al., 2003; Elliot et al., 2003). Now that we have a decent approximation of the date the carbonate was produced we can investigate the effects of using the different (although not statistically different in our salinity range) salinity– $\delta^{18}\text{O}_\text{W}$  relationships (Table 2) and the salinities from the two stations. All calculations using salinity values from the offshore station (PSB003) resulted in average temperature predictions

greater than  $3^{\circ}\text{C}$  warmer than measured (Table 3, Fig. 10). If we assumed that this salinity was correct, we would find the shells to be about  $-1\text{‰}$  out of equilibrium. Elliot et al. (2003) stressed that the offset between their measured and predicted  $\delta^{18}\text{O}_\text{S}$  in some locations was caused by poor salinity– $\delta^{18}\text{O}_\text{W}$  relationships and/or differences in salinity between where the measurement was taken (surface water) and where the clam lived (infaunal). We further stress the importance of this. As in our study, it is quite possible that the disequilibrium patterns discussed in Auclair et al. (2003) would be quite different if the actual  $\delta^{18}\text{O}_\text{W}$  and/or salinity at their site was known (they used salinity from a distant station and a theoretical salinity– $\delta^{18}\text{O}_\text{W}$  relationship). Although Auclair et al. (2003) found their brachiopod shells to be largely out of equilibrium (up to  $-6\text{‰}$ ), a shift of  $1\text{‰}$  in their data would undoubtedly have changed some of their conclusions. However, even using the nearshore salinity data we still calculate average temperatures from  $1.7$  to  $4.4^{\circ}\text{C}$  warmer than measured (based on average  $\delta^{18}\text{O}_\text{S}$  and average instrumental temperature for the period in which the shells grew; Table 3). Averaging the time resolved data can bias the average temperature to warmer temperatures as it can be expected that these shells grow more during the warmer months of the year (i.e., more data points in warmer months will bring the average temperature up). However, both of these sites experience sharp salinity drops, which severely lower the calculated temperature during these periods (See Fig. 10). If these periods are excluded, the

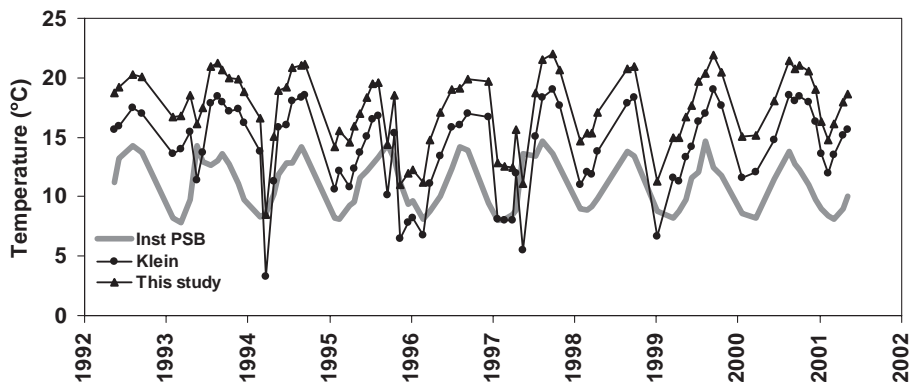


Fig. 10. Comparison between instrumental (Inst PSB, grey line) and calculated temperatures. Calculated temperatures were calculated using the average  $\delta^{18}\text{O}$  from the three shells and salinity from the offshore station. The most extreme salinity– $\delta^{18}\text{O}_\text{W}$  relationships were used (Klein et al., 1996b) and data from this study); calculations using the other relationships lie between the two extremes.

difference between calculated and measured temperature becomes slightly larger (Fig. 10). Therefore, Table 3 is an under-estimation of the difference and not an over-estimation. Interestingly, using the paleotemperature equation of Grossman and Ku (1986), even warmer temperatures are predicted ( $\sim 0.5$  °C). Furthermore, the oxygen isotope fractionation between inorganically precipitated aragonite and water determined by Zhou and Zheng (2003) predicts cooler temperatures than were measured. As stated in their paper, the empirical equations derived for biogenic carbonates reflect a steady-state equilibrium, whereas the inorganic fractionation factors they derived are near thermodynamic equilibrium. As discussed above, we cannot test equilibrium conditions with our data because we do not know the exact  $\delta^{18}\text{O}_\text{W}$ . It remains unknown if *S. giganteus* precipitates out of 'equilibrium' with surrounding water or if the water available to them (e.g., pore water; cf. Elliot et al., 2003) is different from the measured surface waters. Nevertheless, these data clearly illustrate the complications of working with intertidal estuarine animals for paleo-environment reconstruction.

#### 4.3. Carbon isotopes

Early work suggested that the  $\delta^{13}\text{C}_\text{S}$  of biogenic carbonates record  $\delta^{13}\text{C}_\text{DIC}$  (e.g., Mook and Vogel, 1968), but many more recent reports have shown that vital effects seriously complicate the link between  $\delta^{13}\text{C}_\text{S}$  and  $\delta^{13}\text{C}_\text{DIC}$  (e.g., Tanaka et al., 1986; McConnaughey, 1989; McConnaughey et al., 1997; Lorrain et al., 2004). These authors report that  $^{13}\text{C}$  depleted respiratory  $\text{CO}_2$  (i.e., metabolic DIC) is incorporated in the skeleton, thus lowering the  $\delta^{13}\text{C}_\text{S}$ . McConnaughey et al. (1997) reported that aquatic invertebrates typically incorporate less than 10% of carbon from metabolic  $\text{CO}_2$  resulting in a decrease in  $\delta^{13}\text{C}_\text{S}$  of 2‰ or less. According to the inorganic experiments of Romanek et al. (1992), the equilibration  $^{13}\text{C}$  fractionation for aragonite relative to  $\text{HCO}_3^-$  ( $\epsilon_{\text{aragonite-bicarbonate}}$ ) is  $+2.7 \pm 0.6$ ‰. Using the salinity data from the Carkeek station (Fig. 3) and our salinity– $\delta^{13}\text{C}_\text{DIC}$  relationship (Fig. 4) we calculated an approximate average  $\delta^{13}\text{C}_\text{DIC}$ , then added 2.7‰ to derive a predicted  $\delta^{13}\text{C}_\text{S}$ . The average predicted  $\delta^{13}\text{C}_\text{S}$  of  $1.95 \pm 1.15$ ‰ is about 2.5‰ higher than the average measured  $\delta^{13}\text{C}_\text{S}$ , and is close to the depletion reported by others (e.g., 2‰, McConnaughey et al., 1997; Owen et al., 2002).

Furthermore, using average  $\delta^{13}\text{C}_\text{DIC}$ ,  $\delta^{13}\text{C}_\text{S}$  and temperature and a metabolic  $\text{CO}_2$  value of  $-19$ ‰ (*S. giganteus* tissue  $\delta^{13}\text{C}$  measured by Simenstad and Wissmar (1985) in the nearby Hood Canal) we calculated a metabolic contribution to the shell of 13% (using the equation of McConnaughey et al., 1997). Although strong ontogenic decreases in  $\delta^{13}\text{C}_\text{S}$  are evident in other venerids (Elliot et al., 2003; Gillikin, 2005), there does not seem to be a strong decrease in  $\delta^{13}\text{C}_\text{S}$  through the lifetime of *S. giganteus* ( $\delta^{13}\text{C}_\text{S}$  actually becomes slightly more positive through ontogeny in shell 1; Figs. 5 and 7). This indicates that the model proposed by Lorrain et al. (2004), stating that bivalves incorporate increasingly more metabolic DIC through ontogeny, may not be a general model for all bivalves.

As previously stated, our salinity– $\delta^{13}\text{C}_\text{DIC}$  relationship is overly simplistic as  $\delta^{13}\text{C}_\text{DIC}$  is known to have large seasonal fluctuations due to respiration, photosynthesis, carbonate dissolution/precipitation, etc. throughout the year (e.g., Hellings et al., 2001; Bouillon et al., 2003). However, in well flushed estuaries with short residence times,  $\delta^{13}\text{C}_\text{DIC}$  may follow a simple linear relationship with salinity, especially in salinities above 25 (e.g., Surge et al., 2001; Fry, 2002; Gillikin, 2005). Furthermore, it is well known that freshwater input is depleted in  $^{13}\text{C}$  (see our data as well as Hellings et al. (2001) for example). Therefore, a drop in salinity will undoubtedly cause a decrease in  $\delta^{13}\text{C}_\text{DIC}$  (of about 4‰ at our site; see Figs. 3B and 4). Considering the large occasional drops in salinity at our site (Fig. 3) and the lack of strong depletions in shell  $^{13}\text{C}$  and  $^{18}\text{O}$ , it is very unlikely that *S. giganteus* precipitates shell material during periods of reduced salinity.

## 5. Conclusions

*S. giganteus* shell oxygen isotopes are clearly controlled by external environmental factors as indicated by the similarities between the three shells. Although there were differences up to 0.5‰ in high resolution  $\delta^{18}\text{O}_\text{S}$  profiles, the difference in average  $\delta^{18}\text{O}_\text{S}$  was less than half of this (0.19‰) and half of what has been reported in corals (0.4‰; Linsley et al., 1999). This indicates that if  $\delta^{18}\text{O}_\text{W}$  is known, average temperature can be calculated with an uncertainty of  $\sim 0.8$

°C. However, in paleo-environmental studies,  $\delta^{18}\text{O}_\text{W}$  is rarely, if ever, known. Despite the salinity and  $\delta^{18}\text{O}_\text{W}$  data available to us, we were still unable to accurately calculate temperature (Table 3). Carbon on the other hand was more complex, although data are roughly conforming to the idea that about 10% of shell carbon originates from metabolic  $\text{CO}_2$  (McConaughy et al., 1997). Despite this metabolic influence, the general range of  $\delta^{13}\text{C}_\text{S}$  is relatively small (1.9‰) and large changes can be expected at this site (up to 4‰) indicating  $\delta^{13}\text{C}_\text{S}$  can give an insight into the salinity in which the shells grew. Using both  $\delta^{18}\text{O}_\text{S}$  and  $\delta^{13}\text{C}_\text{S}$  as an indication of salinity, it seems that *S. giganteus* do not grow during periods of reduced salinity. We were unable to determine if *S. giganteus* precipitates their shell in isotopic equilibrium with surrounding waters, but these data do clearly highlight some of the problems associated with using intertidal estuarine biogenic carbonates as paleotemperature proxies. Evidentially, salinity independent proxies, or a salinity proxy, are necessary for more precise paleotemperature determinations.

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