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Investigating δ^{13}C and Δ^{14}C within *Mytilus californianus* shells as proxies of upwelling intensity

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[1] Along the west coast of North America, climate and marine productivity is affected by seasonal to interannual changes in coastal upwelling. Our understanding of upwelling variability in the past is limited by the short duration of instrumental records. Changes in upwelling intensity are expected to affect the ^{13}C/^{12}C (δ^{13}C) and radiocarbon (Δ^{14}C) content of marine dissolved inorganic carbon (DIC) due to variable mixing of old, upwelled seawater into surface waters. If seasonal variations in the δ^{13}C of DIC are recorded in marine bivalve shells, they may provide valuable information about the extent of upwelling in the past. Comparison of modern *Mytilus californianus* shells from South California with a 5 year time series of coastal seawater Δ^{14}C and δ^{13}C allows an assessment of the suitability of *Mytilus* shell Δ^{14}C and δ^{13}C as proxies of upwelling intensity. We show that both absolute values and the seasonal range in seawater Δ^{14}C are preserved in shell Δ^{14}C, allowing its use as an indicator of upwelling intensity. Interpretation of shell δ^{13}C is more problematic, with the δ^{13}C of shell carbonate lower than seawater DIC by variable amounts (ranging from 0.5‰ to 1.5‰) due to the incorporation of metabolic carbon. The spatial and temporal variability observed in specimens that grew during the severe El Niño event of 1997–1998 demonstrates how a transect of shells spanning the western North American coastline can be used to reconstruct large-scale patterns of seawater Δ^{14}C variability for specific intervals of interest, such as those associated with El Niño Southern Oscillation–type phenomena.

1. Introduction

[2] Along the west coast of North America, climate and marine productivity are strongly affected by upwelling driven by seasonal offshore winds and associated Ekman transport. The timing and intensity of this seasonal upwelling varies on decadal [*Chhak and Di Lorenzo*, 2007] and shorter time scales [*Legaard and Thomas*, 2007]. Recently, strong El Niño events have led to significantly decreased upwelling, decreased wind-driven mixing, and a weakening of the southward flowing California Current [*Lynn et al.*, 1995; *Bograd and Lynn*, 2001]. The resultant high sea surface temperatures (SSTs) and low nutrient concentrations during these events have significant negative impacts on marine ecosystems [*Chavez et al.*, 2002]. However, our understanding of the complex California Current system, upwelling, rainfall, and El Niño Southern Oscillation, and how these might change due to anthropogenic influences, is currently limited by the short duration of instrumental records.

[3] In order to extend records of upwelling intensity further back in time, we must identify suitable proxies of upwelling intensity. In this study, we examine the suitability of carbon isotope signatures preserved in marine bivalve *Mytilus californianus* (California mussel) shells as potential indicators of upwelling. Increased mixing of upwelled subsurface waters into surface waters results in cooler sea surface temperatures (SSTs), increased salinity and nutrient concentrations, and also changes in the ^{13}C/^{12}C (δ^{13}C) and radiocarbon (Δ^{14}C) signature of dissolved inorganic carbon (DIC). The δ^{13}C of DIC in surface waters tends to be more enriched as a result of increased biological utilization of the light ^{12}C isotope. As this organic matter falls through the water column, some of it is remineralized, which causes the δ^{13}C of DIC to become more depleted with depth. Upwelling should therefore cause the δ^{13}C of DIC in surface waters to become more depleted. Moreover, deeper waters have a lower radiocarbon content (Δ^{14}C) of DIC because they have been isolated from the atmosphere, where radiocarbon (^{14}C) is produced, and over time, their initial ^{14}C will decay radioactively [*Broecker and Peng*, 1982]. During periods of intense upwelling, the mixing of this "old" deeper water with surface water results in a lowr Δ^{14}C of DIC.

[4] Such seasonal changes in the isotopic composition of DIC are incorporated into the calcium carbonate skeletons of marine organisms as they form and so may allow us to reconstruct a history of upwelling and aspects of ocean circulation beyond the availability of instrumental records. Marine radiocarbon is already widely used within corals as a tracer of past ocean circulation and upwelling intensity [e.g., *Druffel*, 2002; *Druffel et al.*, 2007], but large surface corals are restricted to the tropics. In areas outside the tropics, marine mollusk shells show promise as seasonal-resolution archives of upwelling intensity and ocean circulation changes [*Scourse et al.*, 2012; *Wanamaker et al.*, 2012]. However, bivalve shell carbon isotope compositions are complicated by a number of factors, including the contribution of metabolic carbon from respiration [see *McConnaughey and Gillikin*, 2008; *Poulain et al.*, 2010; *Beirne et al.*, 2012, and references therein]. Intrashell radiocarbon studies of marine mollusks from Peru [*Andrus et al.*, 2005; *Jones et al.*, 2007, 2009] and California [*Culleton et al.*, 2006] indicate that seasonal variability in Δ^{14}C is indeed detectable in both prebomb and archaeological shells. Unfortunately, in these studies, there were no time series of seawater DIC Δ^{14}C and δ^{13}C available for direct comparison with the mollusk records. A unique 5 year time series of seawater geochemistry from Newport Beach, CA [*Hinger et al.*, 2010; *Santos et al.*, 2011], allows us to assess whether *M. californianus* from this region accurately record both the absolute values and range in seawater DIC δ^{13}C and Δ^{14}C within their shells. We also present results from *M. californianus* shells collected after the 1997–1998 El Niño event that demonstrate the utility of using shells spanning the North American coastline to generate snapshots of broader geochemical patterns in seawater for specific periods of interest.

2. Materials and Methods

2.1. Seawater Geochemistry and Environmental Data Sets

[5] Biweekly seawater sampling was carried out at Newport Beach Pier, Orange County, CA (33.61°N, 117.93°W), from 2005 to 2011. Detailed methods and the full data sets from 2005 to 2011 are presented in *Hinger et al.* [2010] and *Santos et al.* [2011]. Water temperature was measured at the time of sampling, and salinity measurements were carried out at Scripps Institution of Oceanography. A daily study of seawater geochemistry between October and November 2004 was compared with Santa Ana River discharge
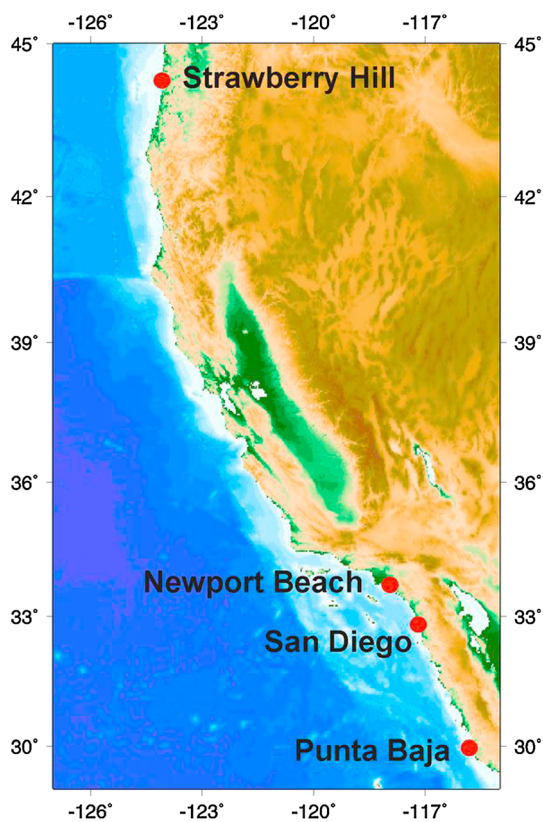
Figure 1. Map showing *Mytilus californianus* sampling sites along the coastline of western North America.

data and wind currents to identify periods when freshwater affected the Newport Beach Pier sampling site [*Hinger et al.*, 2010]. Significant inputs of freshwater appeared to lower the $\delta^{13}C$ and $\Delta^{14}C$ of DIC, as well as reduce salinity. On days where there was no local river input and no precipitation, surface salinity was between 33 and 34. A lower salinity limit of 33 was therefore used to determine seawater samples which were not influenced by freshwater inputs [see *Hinger et al.*, 2010], and these underwent further analysis to produce records of $\delta^{13}C$ and $\Delta^{14}C$ of DIC. Seawater collected for DIC $\Delta^{14}C$ analysis was acidified to produce CO_2 following an established protocol [*McNichol et al.*, 1994]. The CO_2 was then converted to graphite by the hydrogen reduction method [*Santos et al.*, 2004] and analyzed for ^{14}C using accelerator mass spectrometry techniques at the Keck Carbon Cycle Accelerator Mass Spectrometer Facility, University of California, Irvine, CA [*Santos et al.*, 2007]. Additional daily sea surface temperature (SST) data sets for sites where *M. californianus* were collected from Punta Baja (29.875°N, 244.125°E), Newport Beach (33.625°N, 242.125°E), and Strawberry Hill (44.375°N, 235.625°E) were obtained using the Daily Optimum

Interpolation (OI), AVHRR Only, Version 2 data set (available from http://coastwatch.pfeg.noaa.gov/ erddap/griddap/ncdcOisst2). Daily SSTs for San Diego were obtained from the Scripps Pier (32.867°N, 242.743°E).

2.2. *Mytilus* Shell Sampling

[6] *M. californianus* is a species of marine bivalve found along the coast of western North America between Baja California and the Aleutian Islands [*Gosling*, 1992]. These organisms are filter feeders, living from the intertidal zone to about 25 m depth. Individuals can live for several years but often are shorter lived in the intertidal zone, where they are more often damaged by wave action and are exposed to greater predation as well as dessication [*Gosling*, 1992]. *M. californianus* also exhibit highly variable growth rates depending on local factors such as growth position, ocean temperatures, and food availability. Their shells consist of an outer layer of calcite and an inner layer of aragonite precipitated from extrapallial fluid found between the shell edge and the mollusk body tissues and so isolated from seawater [*Wheeler*, 1992]. The composition of this extrapallial fluid can be altered by the bivalve in order to promote calcium carbonate formation, for example, by increasing pH [*Crenshaw*, 1972].

[7] Living *M. californianus* were collected in summer of 2009 and 2010 from the lower intertidal zone (33.60°N, 117.87°W) approximately 2.5 km from Newport Beach Pier, CA, where the seawater for the time series was sampled. Intertidal specimens were also live-collected along the North American coastline in 1998–1999 (Figure 1) from Punta Baja in Mexico and San Diego, CA, and Strawberry Hill, OR, in the United States. These shells allow the investigation of how *M. californianus* shells from a much larger geographic region can be used to examine a particular event—in this case, the strong El Niño event of 1997–1998, which severely disrupted the California Current system and resulted in a collapse of upwelling [*Lynn et al.*, 1998].

2.3. Shell Sampling for $\delta^{13}C$ and $\delta^{18}O$ and Analytical Methods

[8] After collection, the mollusk body tissues were removed by physical scraping and submersion in 15% hydrogen peroxide, replenished periodically, until all visible signs of reaction had ceased. This process also assisted in the removal of the outer organic periostracum layer before milling. One
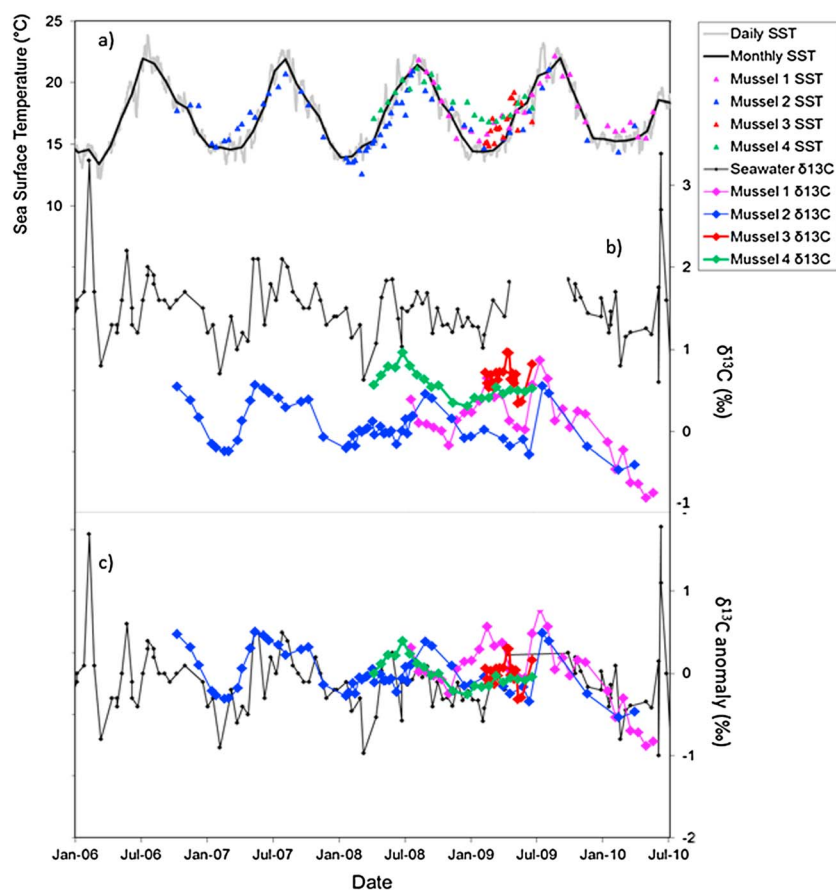
Figure 2. (a) (gray) Daily and (black) monthly average SSTs from Newport Beach, CA. Data are gridded Optimum Interpolation SSTs (OISST-V2-AVHRR) available from the National Climatic Data Center. Colored triangles show the $\delta^{18}O$-reconstructed SSTs [*O'Neil et al.*, 1969] from three individual shells (each in a different color). (b) Seawater $\delta^{13}C$ of DIC from Newport Beach (black line and data points with 1σ error bars [data taken from *Santos et al.*, 2011]). Colored diamonds correspond to seasonal-resolution $\delta^{13}C$ measurements in each of the three individual shells. (c) Shell $\delta^{13}C$ anomaly (individual $\delta^{13}C$ values − mean $\delta^{13}C$ of the shell) shown by colored diamonds, with each color representing a different shell. Also plotted in black is the DIC $\delta^{13}C$ anomaly (individual $\delta^{13}C$ values − mean $\delta^{13}C$ between 2004 and 2009 [all data within *Hinger et al.*, 2010; *Santos et al.*, 2011]).

valve was then sliced along the maximum growth axis, and the cross sections were polished to reveal the growth banding. Consecutive samples were milled parallel to the growth banding from the outer calcite layer of one of the valve cross sections at approximately 100–300 μm resolution to a depth of 300 μm using a New Wave Research Micromill in order to create high-resolution (up to weekly) isotope profiles of oxygen ($\delta^{18}O$) and carbon ($\delta^{13}C$). Approximately 30–60 μg of drilled powder was analyzed for stable oxygen ($\delta^{18}O$) and carbon ($\delta^{13}C$) isotopes using a Kiel IV carbonate device coupled with a Thermo Delta-V isotope ratio mass spectrometer. The uncertainties of $\delta^{13}C$ and $\delta^{18}O$ measurements, determined from routine analysis of certified reference materials (NBS-18 and NBS-19), are 0.06‰ and 0.08‰, respectively.

2.4. Construction of Age Models for *M. californianus* from $\delta^{18}O$-reconstructed SSTs

[9] In order to create an age model for each *M. californianus* shell, high-resolution $\delta^{18}O$ values were converted to SST using the calcite-water $\delta^{18}O$ equilibrium equation defined by *O'Neil et al.* [1969]: SST (°C) = $16.9 - 4.38(\delta^{18}O_{calcite} - \delta^{18}O_{seawater}) + 0.1$ $(\delta^{18}O_{calcite} - \delta^{18}O_{seawater})^2$, where $\delta^{18}O_{calcite}$ and $\delta^{18}O_{seawater}$ are measured in ‰VPDB. As seawater $\delta^{18}O$ values were not available for the period of mollusk growth at each site, a constant seawater $\delta^{18}O$ value was assumed for each location that created a best fit between the maximum and minimum shell $\delta^{18}O$-reconstructed SSTs and the observed SST record (0.67‰ VSMOW at Punta Baja, −0.21‰ VSMOW at San Diego, −0.13‰
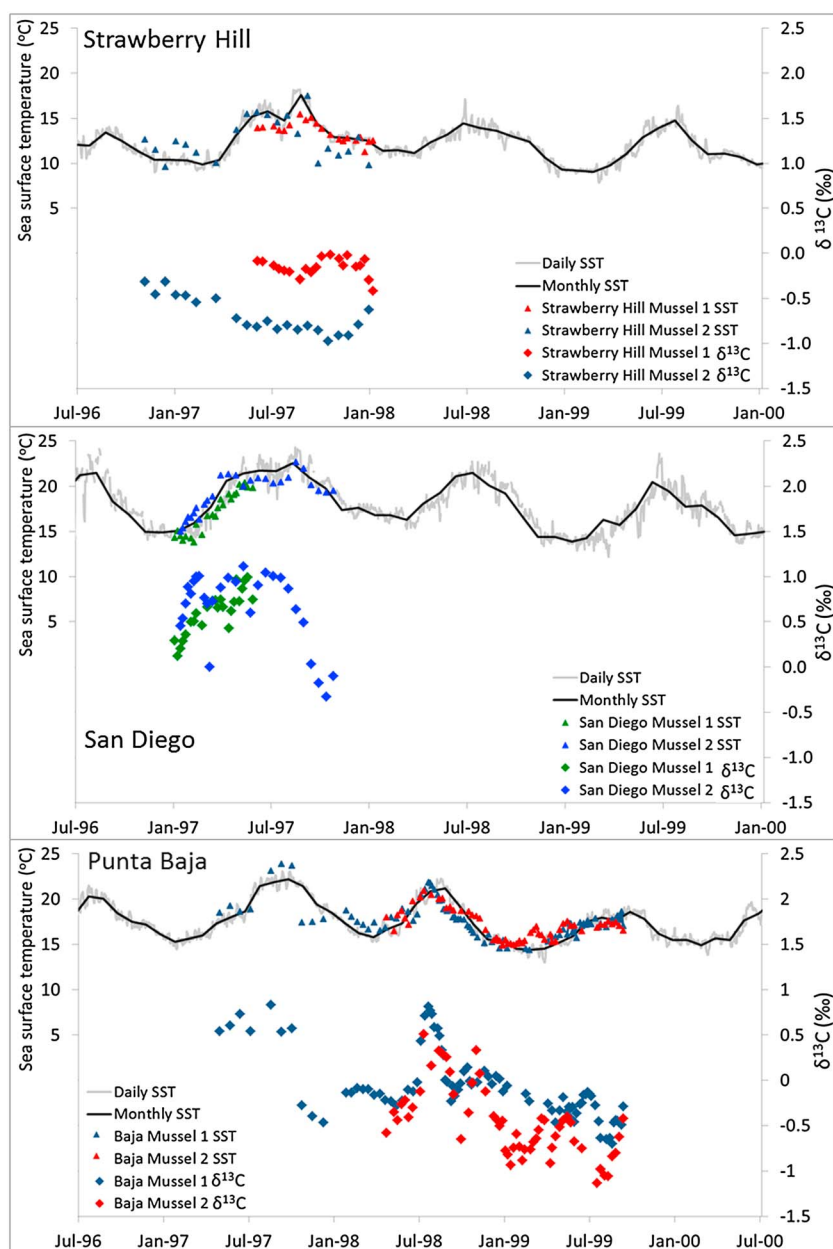
Figure 3. (gray) Daily and (black) monthly average SSTs for (a) Strawberry Hill, OR, (b) San Diego, CA, and (c) Punta Baja, Mexico. Data sets are gridded Optimum Interpolation SSTs (OISST-V2-AVHRR) available from the National Climatic Data Center. Colored triangles in each plot show δ^{18}O-reconstructed SSTs [*O'Neil et al.*, 1969] from individual mussel shells, and colored diamonds are corresponding δ^{13}C values within these shells.

VSMOW at Newport Beach, and 0.06‰ VSMOW at Strawberry Hill). The age models for each shell were then created using the best fit of the reconstructed SSTs to the observed weekly average SSTs and by pinning the end of the reconstructed SST to the appropriate date in the observed SST curve before the collection date.

[10] At all sites, the reconstructed range in SSTs from the shells matched the reconstructed range in

instrumental SSTs (Figures 2–5), implying that shell growth was continuous throughout the year with no growth cessations due to biological or environmental factors. However, the rate of growth often varied between individual mollusks and over each mollusk's lifetime, as would be expected in the variable growth environment of the intertidal zone. Unfortunately, the lack of seawater δ^{18}O at the sampling sites makes it impossible to examine further whether the shells formed out of equilibrium
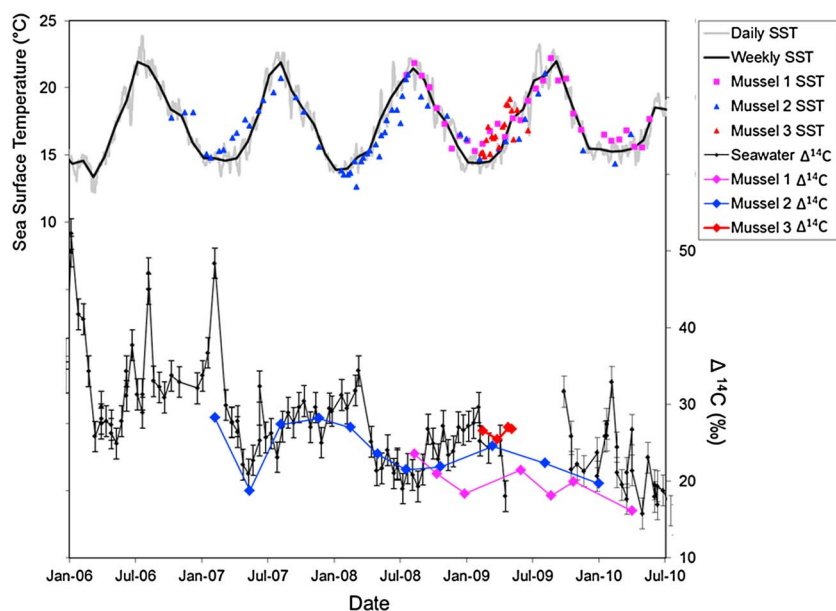
1860

Figure 4. (a) (gray) Daily and (black) monthly average SSTs from Newport Beach, CA. Data are gridded Optimum Interpolation SSTs (OISST-V2-AVHRR) available from the National Climatic Data Center. Colored triangles show the δ^{18}O-reconstructed SSTs [*O'Neil et al.*, 1969] from three individual shells (each in a different color). (b) Seawater Δ^{14}C of DIC from Newport Beach (black line and data points with 1σ error bars [data taken from *Santos et al.*, 2011]). Colored diamonds correspond to seasonal-resolution Δ^{14}C measurements in each of the three individual shells.

with seawater δ^{18}O as recently proposed by *Ford et al.* [2010] using *M. californianus* from San Diego. Nevertheless, the age models were more than adequate for use in sampling to obtain seasonal radiocarbon values.

2.5. Shell Sampling for Δ^{14}C and Analytical Methods

[11] Using the age models generated for each shell, larger, seasonal-resolution samples were then milled parallel to growth banding, but to a greater depth (500 μm), on the mirroring valve cross section for radiocarbon analysis. The 5–10 mg calcite samples were then leached to remove exogenous carbon, converted to graphite, and analyzed by accelerator mass spectrometry (AMS) with an uncertainty of 2‰–3‰ (1σ) [*Beverly et al.*, 2010]. Radiocarbon data are reported here as Δ^{14}C (‰ difference from the ^{14}C/^{12}C ratio in 19th century wood) [*Stuvier and Polach*, 1977].

3. Results

3.1. *M. californianus* δ^{13}C Profiles

[12] Shell δ^{13}C values from Newport Beach range between -0.8‰ and 0.96‰ VPDB and appear to

form weak annual cycles with more depleted values present in winter months and more enriched values during spring and summer months (Figure 2). The shell δ^{13}C values appear to roughly follow the trends visible in the seawater DIC δ^{13}C record but with a negative offset of 0.5‰–1.5‰ (Figure 2). By taking the shell δ^{13}C anomaly profiles (individual δ^{13}C values − mean δ^{13}C of the shell) and comparing these to the DIC δ^{13}C anomaly (individual δ^{13}C values − mean δ^{13}C between 2004 and 2009 [*Santos et al.*, 2011]), it is possible to see that much of the variability in δ^{13}C seen within each shell can be explained by variability in DIC δ^{13}C (Figure 2). However, while similar trends are often present between individual shell δ^{13}C profiles, the absolute δ^{13}C values in different shells are up to 1‰ from each other.

[13] It is not possible to identify whether similar patterns between seawater DIC δ^{13}C and *Mytilus* shell δ^{13}C exist from the shells sampled in the other locations due to a lack of suitable seawater DIC δ^{13}C measurements at other sites. Trends often appear similar between individual shells in each site, but, again, there are also significant differences, and absolute values are different by up to 1‰, for example, at the Strawberry Hill site (Figure 3). There is no overall geographic
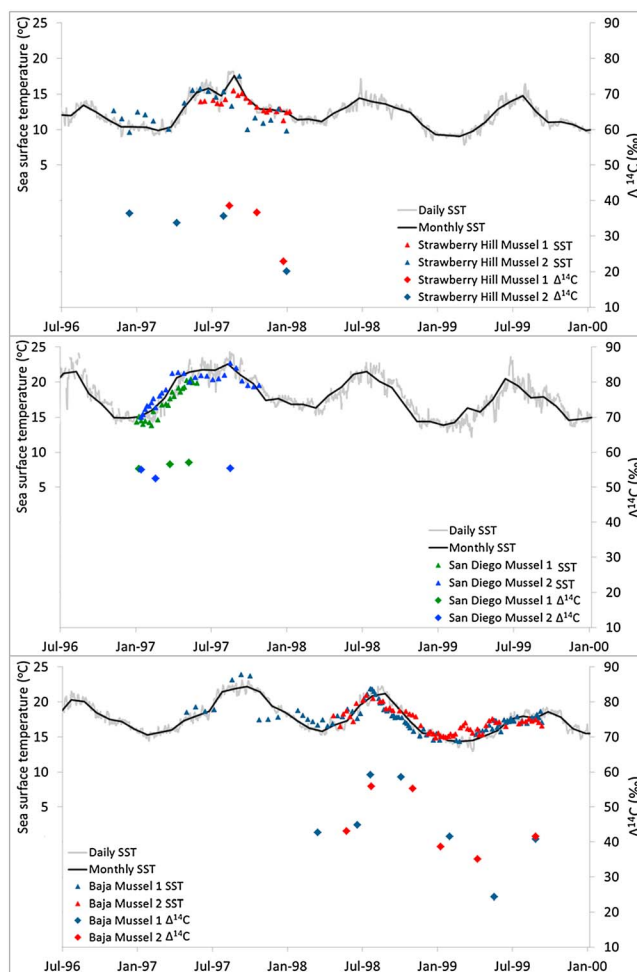
Figure 5. (gray) Daily (black) and monthly average SSTs for (a) Strawberry Hill, OR, (b) San Diego, CA, and (c) Punta Baja, Mexico. Data sets are gridded Optimum Interpolation SSTs (OISST-V2-AVHRR) available from the National Climatic Data Center. Colored triangles in each plot show δ¹⁸O-reconstructed SSTs [*O'Neil et al.*, 1969] from individual mussel shells, and colored diamonds are corresponding seasonal Δ¹⁴C values within these shells.

pattern present in the absolute δ¹³C values from Oregon (ranging from −0.98‰ to −0.06‰ VPDB) to Mexico (ranging from −1.13‰ to 0.84‰ VPDB) apart from a suggestion that colder temperatures may be associated with more depleted δ¹³C values (Figure 3).

3.2. Intrashell Radiocarbon Measurements in *M. californianus*

[14] Δ¹⁴C values of mussel shells from Newport Beach show seasonal-scale variability and range from 16‰ to 28‰ (see Table SS1 of auxiliary material)[1]. The Δ¹⁴C values and seasonal vari-

ability seen within the shells match very well with the observed seawater DIC Δ¹⁴C measurements made during the same time interval [*Santos et al.*, 2011] (Figure 4). However, Δ¹⁴C values in late 2009 and 2010 are 5‰–10‰ lower than the seawater DIC Δ¹⁴C measurements made during this time.

[15] Seasonal-scale Δ¹⁴C changes are also visible in mussel shells collected from Strawberry Hill, OR, and Punta Baja, Mexico, after the 1997–1998 El Niño event (Figure 5). Δ¹⁴C shell values range from 20‰ to 38‰ at Strawberry Hill and from 24‰ to 59‰ at Punta Baja (Table SS1). Only short records (6–9 months) were obtained from shells collected in San Diego, which may explain why no seasonal variability in Δ¹⁴C is seen in these shells with values only ranging from 52‰ to 57‰ (Figure 5).

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[1]Additional supporting information may be found in the online version of this article.

4. Discussion

4.1. Controls on δ^{13}C in *M. californianus* Shells

[16] The use of marine mollusk δ^{13}C to infer paleoenvironmental information has proved challenging due to the uncertainties in the extent of the contribution of metabolic, isotopically light, carbon, which can be incorporated into the shell via the extrapallial fluid [*McConnaughey and Gillikin*, 2008], as well as the numerous environmental controls on δ^{13}C of DIC, such as ocean circulation and productivity. Various studies have concluded that the fraction of respired carbon incorporated into the shell is approximately 10% in *Mytilus* shells [*Gillikin et al.*, 2006] and other bivalve species [*Lorrain et al.*, 2004; *McConnaughey et al.*, 1997]. However, differences in mollusk metabolic rate over the year, as they age, and between individuals continue to make quantitative use of mollusk shell δ^{13}C as a proxy problematic [see *McConnaughey and Gillikin*, 2008; *Beirne et al.*, 2012; *Poulain et al.*, 2010, and references therein]. The differences observed between seawater DIC δ^{13}C and *M. californianus* shell δ^{13}C at Newport Beach (Figure 2) confirm that *Mytilus* shells are not directly recording seawater DIC δ^{13}C. δ^{13}C of inorganic calcite is enriched by over 1‰ compared to δ^{13}C of DIC [*Romanek et al.*, 1992], and so the negative offset of approximately 1‰ observed between the mussel shell calcite and seawater DIC indicates an offset from equilibrium values of over 2‰. The isotopic disequilibrium seen is unlikely to be due to kinetic fractionation because this would alter both δ^{18}O and δ^{13}C [*McConnaughey et al.*, 1997], and the δ^{18}O of the specimens we studied appears to be in equilibrium with seawater δ^{18}O. Instead, the variable negative offset observed is likely to be due to the input of isotopically light metabolic carbon. These issues, along with the inconsistent relationship between seawater DIC δ^{13}C and upwelling intensity off South California [*Hinger et al.*, 2010; *Santos et al.*, 2011], and differences of up to 1‰ between individuals growing at the same time indicate that *Mytilus* shell δ^{13}C records will prove challenging to use as a quantitative proxy of upwelling intensity in this region and likely elsewhere. This is in contrast with the much earlier work of *Killingley and Berger* [1979], who suggested that δ^{13}C within mussel shells could be used to identify the onset and duration of upwelling episodes. The δ^{13}C profiles from San Diego in 1998, while short in duration, also do not show the consistent pattern predicted by *Killingley and Berger* [1979].

4.2. Potential of *Mytilus* Shell Δ^{14}C as a Proxy of Upwelling Intensity

[17] The excellent match between shell and seawater DIC Δ^{14}C values from Newport Beach (Figure 4) indicates that *M. californianus* shells show great potential as archives of high-resolution seawater DIC Δ^{14}C outside the range of tropical surface corals, where extremely little high-resolution data presently exist. Such records would allow further investigation of ocean circulation and upwelling changes and their role in global climate and the carbon cycle [*Culleton et al.*, 2006]. *Mytilus* shells could be also used as a cheaper, quicker, and logistically easier alternative to frequent seawater sampling in order to create DIC Δ^{14}C time series at coastlines around the world. Marine mollusk shells effectively time average seawater DIC Δ^{14}C which will be more reflective of the average values than spot seawater measurements. Shell carbonate samples are also easier to collect, store, and analyze for radiocarbon. *Mytilus* shell Δ^{14}C records are relatively short (a few years) compared to the hundreds of years possible with large tropical corals or other deeper-dwelling and longer-lived bivalves, such as *Arctica islandica* [*Wanamaker et al.*, 2012], but mussel shells do allow snapshots of seawater Δ^{14}C over large geographic areas. Older intertidal and shallow mollusk shells, such as *Mytilus*, are also easier to obtain than fossil corals because they have been used by humans for food for many thousands of years and hundreds of thousands of shells can be found in middens along coastlines around the world [*Álvarez et al.*, 2011]. Subtidal *Mytilus* shells would likely have larger growth rates and longer life spans and could generate longer Δ^{14}C records, especially in generating modern seawater DIC Δ^{14}C time series, but are less well represented in museum collections and archaeological sites.

4.3. Demonstration of the Utility of *Mytilus* Shell ^{14}C to Reconstruct Seasonal Seawater ^{14}C Following the 1997–1998 El Niño Event

[18] *Mytilus* shells were collected from along the west coast of North America after the El Niño event of 1997–1998 that severely disrupted the California Current system and resulted in a collapse of upwelling. This event provides an ideal opportunity to assess the utility of a transect of mussel shells in reconstructing the intensity and regional expression of particular events. Unfortunately, the records from these small, intertidal shells are often too short to allow a clear view of how the El Niño event differed from normal conditions in preceding years but still offer interesting glimpses into changes in upwelling intensity over this period along the coastline.

[19] It would appear that more enriched values, indicative of surface seawater with little vertical mixing, are present in more southern sites during 1997 and 1998 and may be attributed to the collapse of upwelling in the California Current associated with the El Niño event [*Lynn et al.*, 1998]. Lower $\Delta^{14}C$ values (~20‰) present in Strawberry Hill in early 1998 imply increased mixing of "old" deeper waters into surface waters. A resumption of upwelling is thought to have occurred during spring of 1998 [*Lynn et al.*, 1998], and uncertainties in the age model may contribute to the lowering of shell $\Delta^{14}C$ values being slightly earlier in this case. The longer $\Delta^{14}C$ records generated from shells from Punta Baja appear to show two periods of upwelling. The first, weaker, period occurs in the spring of 1998 toward the end of the El Niño event and the second, stronger, upwelling period in the late spring of 1999 (Figure 5). This would be consistent with the Bakun upwelling index anomalies along the coast expected for this latitude [*Bograd et al.*, 2000]. The lack of a change in shell $\Delta^{14}C$ in San Diego from winter 1996/1997 to autumn of 1997 makes these records difficult to interpret. However, this time period spans the usual period of maximum upwelling in spring and may reflect a collapse of upwelling associated with the 1997/1998 El Niño event or instead consistent upwelling intensity over the entire period. The upwelling signal in the South California Bight, including San Diego and Newport Beach, is also not as large as in other, less oceanographically complex, areas of the North American coastlines [*Santos et al.*, 2011].

[20] Data sets such as this [e.g., *Scourse et al.*, 2012; *Wanamaker et al.*, 2012], spanning large geographic areas, would be also of significant assistance in testing and refining ocean models which are increasingly incorporating ocean tracers. Given the importance of the oceans to the global carbon cycle, it is important that models are able to accurately represent ocean circulation and mixing patterns as well as air-sea gas exchange, so that we can address questions about the interactions of the ocean and atmosphere both in the future and the past. Radiocarbon is one of several ocean circulation tracers which has huge potential to be used to assess model performance, and so further data sets using new methods such as this could be of great benefit.

5. Conclusions

[21] The variable negative offset between *M. californianus* $\delta^{13}C$ and measured seawater DIC $\delta^{13}C$ from South California, as well as the lack of a consistent relationship between seawater DIC $\delta^{13}C$ and upwelling, indicate that it will prove difficult to use *Mytilus* shell $\delta^{13}C$ as a quantitative proxy of upwelling and ocean circulation in this region. This is likely primarily due to the small but variable contribution of respired, isotopically light, carbon to *Mytilus* shells.

[22] Comparison of modern *M. californianus* shells from South California with a unique coastal 5 year time series of seawater $\Delta^{14}C$ demonstrates that the absolute values and full range of seasonal variability in seawater $\Delta^{14}C$ is recorded within the shells. Seasonal reconstruction of seawater DIC $\Delta^{14}C$, and therefore upwelling intensity, is therefore possible where growth rates are fast enough to allow seasonal resolution sampling and where no growth stops occur due to environmental limits on growth.

[23] The spatial and temporal variability visible in *Mytilus* shells collected in 1998–1999 demonstrates how modern mussel shells spanning the western North American coastline could be used to reconstruct large-scale patterns of seawater $\Delta^{14}C$ variability for specific intervals of interest in the past or even for creating ongoing time series of seawater $\Delta^{14}C$. This would not only increase our understanding of the complex interactions between surface and deepwater masses in this region, but such data sets would be also of huge benefit in ocean model testing and development.

Acknowledgments

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