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The Effects of Heating on $\delta^{18}O$ and $\delta^{13}C$ in *Mytilus californianus* Shell Carbonate: Implications for Paleoenvironmental Reconstruction and Season of Harvest

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The use of stable oxygen ($\delta^{18}O$) and carbon ($\delta^{13}C$) isotopic ratios of marine shell carbonate is a powerful tool for reconstructing past sea surface temperatures (SST) and estimating season of harvest for shells from coastal archaeological sites. While methods for sampling shells and analyzing the resulting data are established, less is known about the effects of anthropogenic activity on the geochemistry of the shells. Through an experimental study in which we heat carbonate powder from Mytilus californianus *shells, we show that mussels cooked by boiling or steaming were unlikely to have their isotopic composition altered by the process. Shells heated over coals, however, show evidence of both visible and structural changes and in some cases are depleted in $\delta^{13}C$ and/or $\delta^{18}O$. This indicates that archaeologists should use caution in interpreting past SST or site seasonality from burned shells and should instead test intact, unburned shells.*

Reconstructing past environments using dietary refuse from archaeological sites is especially valuable for understanding human-environment interactions because it eliminates the need to reconcile different time scales between human activities and environmental changes. By analyzing faunal remains from archaeological sites, for example, we know that any reconstructed environmental attributes represent the context in which people performed those activities and we can discover the subsistence activities associated with the sample. This is one of the strengths of archaeology, which is positioned to model medium- or long-term environmental change and its relationship to cultural contexts (e.g., van der Leeuw and Redman 2002). That relationship is especially pertinent in the case of geochemical methods, including studies using stable isotopic measurements, which can be used to model environmental change with low or high resolution (e.g., Kennett et al. 2012; Kennett and Kennett 2000) before being associated temporally with the archaeological record. It is for this reason that analyses using stable isotopic measurements of carbon ($\delta^{13}C$), nitrogen ($\delta^{15}N$), oxygen ($\delta^{18}O$), sulfur ($\delta^{34}S$), and strontium ($\delta^{87}Sr$) from a variety of organic and inorganic materials have become more prominent in the archaeological literature in studies designed to address a variety of research questions (e.g., Bentley et al. 2004; Blanz et al. 2019; Curto et al. 2019; Eerkens et al. 2016; Evans et al. 2006; Hamilton et al. 2019; Hodell et al. 1995; Kennett et al. 2012; Kennett and Kennett 2000; Price et al. 2019; Richards et al. 2001; Rose et al. 2019; Walker and DeNiro 1986; Wright 2005).

One of the most common paleoenvironmental tests used by archaeologists in coastal environments is the analysis of $\delta^{13}C$ and $\delta^{18}O$ in carbonate from marine mollusk shells to reconstruct past sea surface temperatures (e.g., Glassow et al. 1994, 2012; Jazwa et

al. 2012; Kennett 1998, 2005) and estimate season of harvest. The latter has implications for the seasonality of site occupation (e.g., Culleton et al. 2009; Eerkens et al. 2013; Jazwa and Kennett 2016; Jazwa et al. 2015; Jew et al. 2013a, 2013b; Kennett and Voorhies 1996; Thakar 2014). Substantial early work was done to determine the relationship between ambient water temperature, water $\delta^{18}O$ (including salinity), and $\delta^{18}O$ values of shell carbonate (Epstein et al. 1951, 1953; Grossman and Ku 1986; Horibe and Oba 1972). More recent work has used these measurements to estimate season of harvest (Culleton et al. 2009; Kennett and Voorhies 1996; Killingley 1981; Jazwa and Kennett 2016; Jew et al. 2013a, 2013b; Shackleton 1973; Thakar 2014) and the intensity of past upwelling events (e.g., Sadler et al. 2012).

Here, we present the results of an experiment to test an important anthropogenic factor that should be taken into account when interpreting isotopic measurements of shell carbonate—the effect of cooking on the $\delta^{13}C$ and $\delta^{18}O$ values of shells. Although some gastropod species like abalone (Colligan et al. 2015; Jazwa et al. 2015) and some bivalves including oysters are typically removed from the shell and processed raw, most other bivalves are most efficiently processed by heating them until the shells open (e.g., Bettinger et al. 1997; Bird and Bliege Bird 1997, 2000; Gifford 1939; Jazwa et al. 2015; Jones and Richman 1995; Kroeber and Barrett 1960). It is important to consider whether the process of heating shells in cooking alters the $\delta^{13}C$ or $\delta^{18}O$ values of the shell carbonate in mollusk shells, and if so whether those changes are consistent and predictable or patchy and random. Previous studies (Milano et al. 2016; Müller et al. 2017) have noted that heating shells can alter their isotopic composition. The species that were tested had shells composed of carbonate with aragonite mineralogy, which can reform into calcite when heated (Gill et al. 1995). We instead focus here on California mussel (*Mytilus californianus*), in which the outer and inner prismatic carbonate layers of the shell already consist of calcite, to determine whether heating can alter $\delta^{13}C$ and $\delta^{18}O$ values. We test the effects of cooking California mussel shells on shell isotopic composition using five different heating methods, and discuss the implications of the results for efforts to reconstruct past patterns of sea surface temperature (SST) fluctuations and interpretations about the season of harvest.

ISOTOPIC ANALYSIS OF *MYTILUS CALIFORNIANUS* SHELL CARBONATE

California mussels are among the most frequently used mollusks for stable isotopic analysis in sites along the Pacific Coast of North America, largely because of their abundance in rocky intertidal zones and in archaeological shell middens (e.g., Bettinger et al. 1997; Coe and Fox 1942, 1944; Glassow et al. 1994; Jazwa 2015; Jazwa et al. 2012, 2015; Jew et al. 2013a, 2013b; Jones and Richman 1995; Suchanek 1981; Thakar 2014). As with other marine shells, oxygen isotopic ratios in the shell carbonate from mussels provide information about the ambient physical and chemical environment during a shell's growth, with new growth bands not affecting previously deposited carbonate. Therefore, they can be sampled at consistent increments along the outer shell to measure fluctuations in $\delta^{13}C$ and $\delta^{18}O$ over the lifetime of the individual mollusk. The two primary factors that contribute to the $\delta^{18}O$ values of the shell carbonate are water temperature and the $\delta^{18}O$ value of ambient seawater, which includes salinity (Wefer and Berger 1991). We assume that the $\delta^{18}O$ composition of the shells reflects variation in SST (Urey 1947). Although salinity in coastal environments can vary seasonally with the amount of riverine input, there are no large rivers on Santa Rosa Island or on the adjacent islands that would alter seawater $\delta^{18}O$, which in this context we treat as constant throughout the year.

Shackleton (1973) showed that for appropriate species, by sampling a shell along its growth axis, it is possible to track the sinusoidal pattern of $\delta^{18}O$ values over the lifetime of the individual. This can be used to estimate the annual range and variability in SST (Epstein et al. 1951, 1953; Horibe and Oba 1972). Shackleton (1973) outlined six ideal criteria that allow the accurate estimation of seasonal variation in SST and the ability to assign season of harvest from individual shells, criteria which we summarize and update here: (a) the species must deposit carbonate in such a manner that its isotopic composition varies with temperature in a way that can be modeled; (b) the isotopic composition of the water must remain consistent or well constrained throughout the year; (c) the new shell must be deposited at the temperature of the water body of interest; (d) the shell must deposit carbonate throughout the year; (e) the growth rate must be sufficient to permit discrete increments; and (f) SST in the location should undergo a reasonably

large and regular seasonal temperature variation. For criterion (a), a series of equations have been previously developed (e.g., Epstein et al. 1951, 1953; Horibe and Oba 1972). Which equation is chosen is not important for the method's development as long as water temperature can be calculated. In this study, we add a seventh criterion: (g) anthropogenic or natural processes should not alter the $\delta^{18}O$ values of the shell carbonate after growth. Any alterations to $\delta^{18}O$ should be minimal and consistent so as to not influence the timing of the seasonal fluctuations in the isotopic composition of the shell.

After a shell has been deposited in a midden and enters the archaeological record, the $\delta^{13}C$ and $\delta^{18}O$ values of the carbonate may be altered by diagenesis of the shell through the intrusion of carbonate from ambient carbon dioxide and water (e.g., Robbins and Ostrom 1995). Furthermore, Gill et al. (1995) has showed that $\delta^{13}C$ and $\delta^{18}O$ values in aragonite can be altered while samples are being drilled. To mitigate these effects, it is common to drill at low speeds and to etch away the outside of the drilled shell powder using a weak acid for radiocarbon or isotopic analysis (UC Irvine 2008). However, it is also necessary to consider the effects of human activities on the isotopic composition of the shell carbonate, particularly the effects of heating shells by cooking.

Andrus and Crowe (2002) conducted a similar study on fish otoliths. They captured specimens of two different fish species and removed the left sagittal otolith from each as control samples prior to heating. They then heated the remaining fish in five ways: direct burning in hardwood coals, roasting over hardwood coals (~200ºC), roasting in a dry oven (150ºC), boiling in seawater, and boiling in fresh water. Andrus and Crowe then tested both the heated and unheated otoliths and found that only burning altered the $\delta^{13}C$ and $\delta^{18}O$ values appreciably. Although they were not able to conclusively attribute the reduction in their measured values to a specific process, they hypothesized that isotopic exchange occurred between atmospheric CO_2 and H_2O and the carbonate during the reaction that converted aragonite to calcite (Andrus and Crowe 2002), mirroring what Epstein et al. (1953) observed when roasting mollusk shells composed of aragonite. Experiments by Milano et al. (2016) and Müller et al. (2017) that subjected shell aragonite to higher temperatures consistently resulted in decreased isotopic values during the transition to calcite. Nonetheless, the carbonate in the outer and inner prismatic layers of *M. californianus* is calcite (Dodd 1964; Glassow et al. 1994), so we do not necessarily expect a similar reaction to occur when these shells are heated.

EXPECTATIONS OF COOKING SHELLS IN THE ARCHAEOLOGICAL RECORD

Mussels and other shell species must be processed prior to being consumed. In the case of species like oysters and some clams, they need only to be removed from their shell and eaten raw. Other species of shellfish (including mussels) are typically cooked before they are eaten. They open naturally when heated, making this essentially the only step in processing. Although experimental tests have been carried out to determine the return rates of processing California mussels raw (Jones and Richman 1995; Noet and Jones 2019), our observations on the relative ease of processing mussels by cooking and the difficulty of managing and cooking raw mussel meat outside of the shell makes it likely that native Californians cooked mussels in the shell in almost all cases.

The two most common methods for cooking bivalves, including mussels, are to roast or boil them until the shells open (e.g., Bird and Bliege Bird 1997, 2000; Gifford 1939; Kroeber and Barrett 1960; Meehan 1982). In their summary of Chumash cooking methods, drawn from Harrington's field notes, Hudson and Blackburn (1983) do not discuss cooking mussels in detail, but further north, Gifford (1939:315) observed that the Coast Yuki typically cooked mussels by placing them on hot coals to open and then left them to dry. Similarly, Kroeber and Barrett (1960:112–113) summarized the cooking practices of several coastal groups, including the Tolowa and Mattole, who typically roasted mussels over coals and then dried them if they were not to be eaten immediately. These ethnographic observations suggest that if we are to reconstruct patterns of past SST and season of harvest, it is important to understand the response of $\delta^{13}C$ and $\delta^{18}O$ in California mussel shell carbonate to cooking using different methods and at different temperatures.

Furthermore, ethnographic accounts suggest that in some cases the time and energy devoted to shellfish harvesting in California may have varied seasonally. In his discussion of Chumash seasonal subsistence rounds, Tartaglia (1976:43) summarized several ethnographic

accounts that included observations on winter shellfish collecting stations and an emphasis on shellfishing during that season, when other foods were less readily available (Landberg 1965). Similar observations were made elsewhere in California (Gifford 1939). Other California groups, including the Yurok, took mussels year-round when the tides permitted (Kroeber and Barrett 1960). For these reasons, efforts to estimate the season of mussel harvesting from archaeological contexts are a useful undertaking when reconstructing past diets and settlement systems.

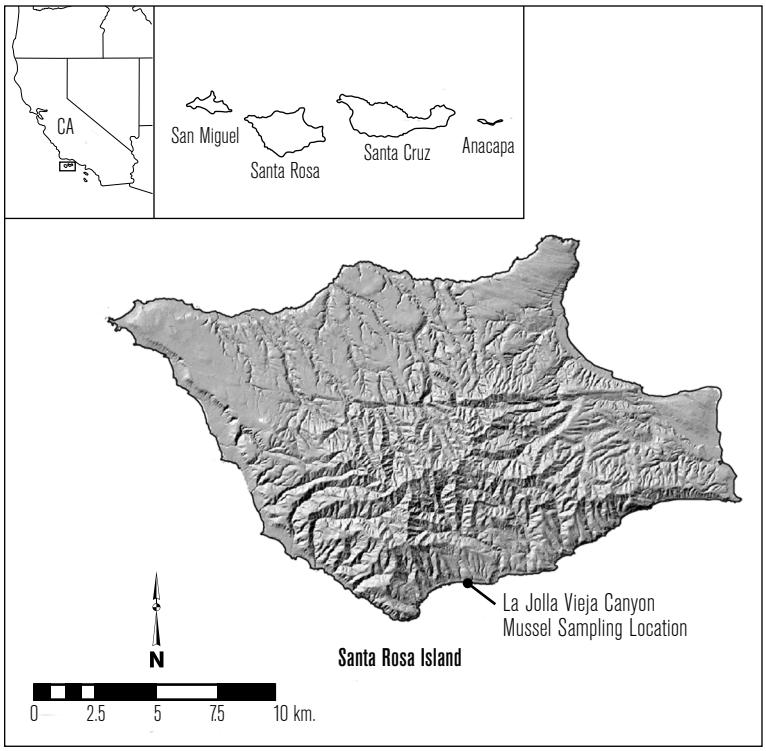

Figure 1. Santa Rosa Island, with the *M. californianus* sampling location to the west of the mouth of La Jolla Vieja Canyon indicated.

METHODS

The central objective of the experiment described in this paper is to assess the effects of heating on the $\delta^{13}C$ and $\delta^{18}O$ values of the carbonate in the prismatic calcite layers of *M. californianus* shells. To simulate ethnographic cooking methods, we processed samples by boiling/steaming and roasting them on coals. We also heated samples using a Thermo Scientific Thermolyne benchtop muffle furnace to determine their response at controlled temperatures.

Shell Harvesting

All of the samples tested in this analysis were from modern *M. californianus* shells harvested at the mouth of La Jolla Vieja Canyon on the southern coast of Santa Rosa Island, one of the four northern Channel Islands in the Santa Barbara Channel (Fig. 1). The sampling location is a wide, flat, gently-sloping sandstone shelf with a dense intertidal community dominated by *M. californianus* and to a lesser extent *Tegula funebralis* (black turban snails; Fig. 2). Compared to other intertidal areas on Santa Rosa Island, the recovery of *Haliotis cracherodii* (black abalone) has occurred quickly in the past five years near La Jolla Vieja, attesting to the availability of nutrients and the health of the intertidal community there.

Figure 2. The rocky intertidal zone where the samples were collected, facing southwest.

The shells included in this analysis were collected on two occasions: six shells were collected by Cause Hanna from the California State University Channel Islands Field Station on January 17, 2016 and 13 shells were collected by Jazwa on March 23, 2017. We used a dull knife to remove barnacles (*Balanus* sp.) and small limpets (*Acmaea* sp.), and to pry the shells open and scrape out the meat. At National Park Service housing, we cut off byssal threads with scissors, washed out the shells using tap water, and left the shells to dry overnight. They were then individually bagged and brought back to either the Human Paleoecology and Isotope Geochemistry

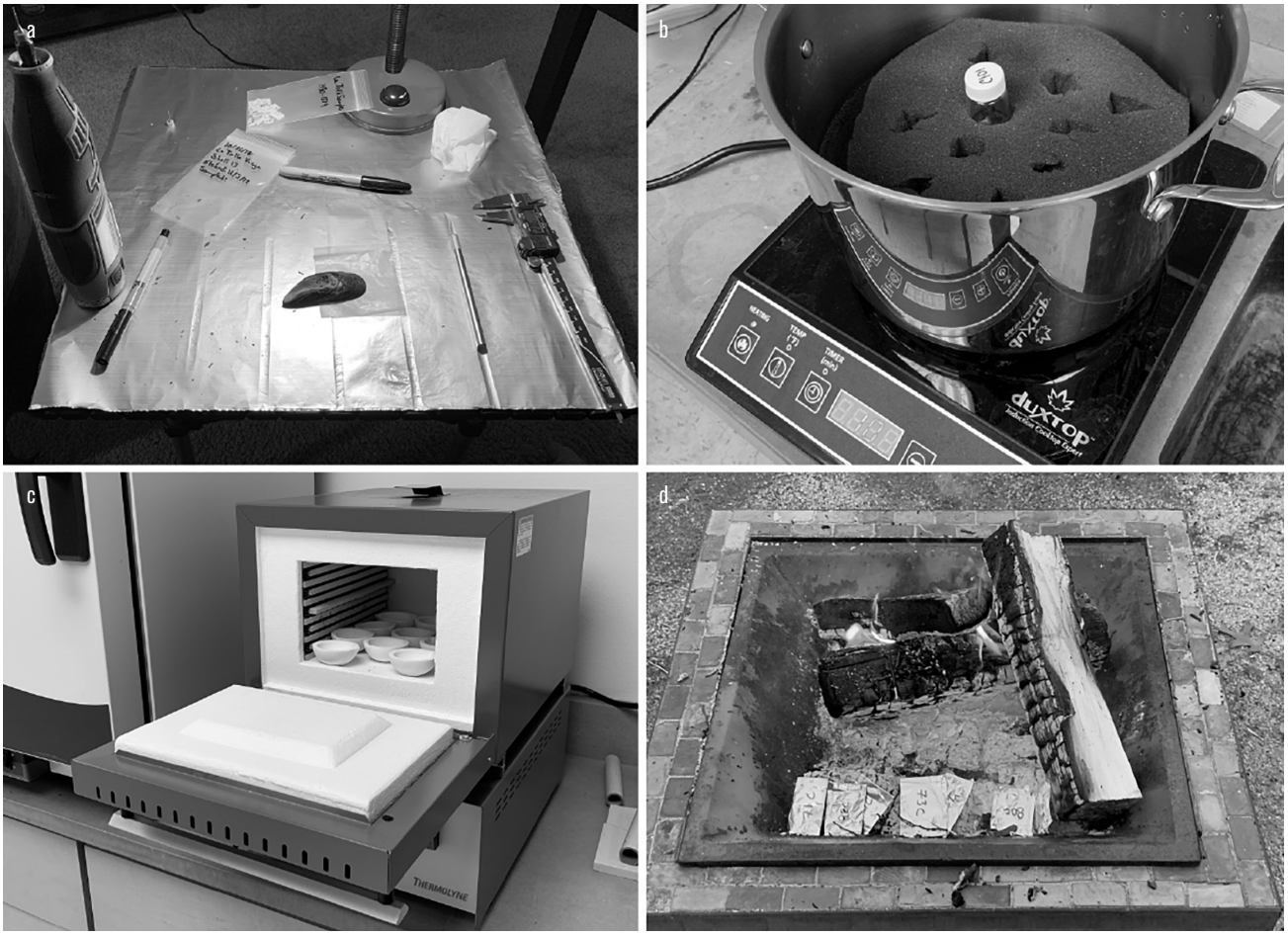

Figure 3. Images representing the primary experimental steps: (a) a characteristic sample drilling kit, including calipers and a Dremel tool; (b) an induction cooktop used for boiling shell powder in scintillation vials; (c) a muffle furnace with samples in ceramic crucibles; and (d) a campfire with samples in foil envelopes being heated by coals.

Laboratory at Pennsylvania State University (PSU; January 2016 shells) or the Human Paleoecology and Archaeometry Laboratory at the University of Nevada, Reno (UNR; March 2017 shells).

Laboratory Sampling and Analysis

Shells selected for this analysis had to meet two primary criteria: (1) the outside calcite layers of the shell were intact within the area of the shell sampled for the analysis (i.e., from the terminal growth band extending toward the umbo) and not damaged from contact with other shells in the water; and (2) they were between 5 and 8 cm. in length. Coe and Fox (1942) measured the rate of growth in *M. californianus* shells and found that shells less than 5 cm. in length grow quickly, but at highly variable rates, while shells 8 cm. or longer grow much more slowly. Shells between 5 and 8 cm. in length grow between 32 and 36 mm. per year on average, and therefore patterns can be compared between them. Furthermore, because the shells for this analysis were collected live rather than from archaeological sites, they were still partially covered by their organic periostracum (outer coating; Dodd 1964), which always decomposes in shell middens. We used a Dremel tool with a 0.8 mm. drill bit to abrade this coating along the growth axis where the shells were to be drilled.

All of the shells were subjected to a 10% HCl bath in a 0.2 N solution at 70ºC, rinsed twice in deionized water, and left overnight in a drying oven at 70ºC. Shells were then drilled at 2 mm. increments from the terminal growth band along the growth axis using a Dremel tool with a 0.8 mm. drill bit (Fig. 3a). Care was taken to only drill the calcite layers of the shell, since the inner nacreous aragonite layers are not deposited in bands that reflect changes through time (Dodd 1964).

The shells harvested in March 2017 were etched and drilled at UNR. Two shells (nos. 1 and 3) had 20 samples taken 0 to 38 mm. from the terminal growth band, one (no. 2) had 10 samples taken 0 to 18 mm. from the terminal growth band, and the remaining ten shells were sampled five times from 0 to 8 mm. from the terminal band. Samples were approximately 0.5 mg. in weight. The powder was then homogenized to ensure that the analysis would not be affected by short term variations in sea surface temperature in the shell and then split in half. The control half was packed into folded weighing paper. The second half of each sample was heated in one of five different ways, with each method performed on 20 powder samples. These samples were placed in scintillation vials and steamed (at ~100ºC) for 30 minutes (Fig. 3b), heated in ceramic crucibles in a muffle furnace for 30 minutes at 150ºC, 250ºC, or 350ºC (Fig. 3c), or placed on coals in an aluminum foil envelope at the edge of a campfire (Fig. 3d). While we were unable to accurately measure the temperature of the coals, it was probably less than 350ºC. The powder was then packed in the same way as the control samples. All samples were submitted to the Yale Analytical and Stable Isotope Center where they were analyzed on a Thermo DeltaPlus XP and a GasBench with analytical error for $\delta^{13}C$ and $\delta^{18}O$ of ± 0.06‰ (VPDB).

As a second experiment, six shells which had been harvested in January 2016 were steamed as whole shells rather than as powder. While this risked not sampling material before and after heating from deposits corresponding to exactly the same range of days, it was more representative of how the shells would have been cooked in the past—as whole shells rather than as shell powder. Five samples from each shell were first drilled at PSU (0–8 mm. from the terminal growth band). The resulting powder was weighed into cups in a custom-made sample mailer with target weights of 0.09 ± 0.01 mg. The shells were then steamed for 30 minutes approximately 5 cm. above boiling tap water (~100ºC). They were then drilled adjacent to the previous samples and the powder was packed in the same way, yielding 30 pairs of samples. All of these samples were submitted for analysis to the Union College Department of Geology Stable Isotope Lab, where they were tested with a Thermo Gas Bench II connected to a Thermo Delta Advantage mass spectrometer in continuous flow mode, with an uncertainty for $\delta^{13}C$ and $\delta^{18}O$ of ± 0.06‰ (VPDB).

Macroscopic and Microscopic Analysis of Shell Appearance

One full *M. californianus* shell was processed during tests of each of the heating methods for macroscopic and microscopic examination alongside the drilled shell powder. Determining structural changes in the shells under different heating regimes could help to identify shells in the archaeological record that might have been heated and help identify which cooking method was used. Each of the shells heated during the experiment was photographed using the camera in an iPhone 10S to observe macroscopic changes. To assess any microscopic changes in a shell upon heating, we broke the shell into small pieces to create a flat surface for viewing and then recorded the images at 20× magnification using an Olympus BX-51TF Research Microscope.

RESULTS

Visual and Structural Effects of Heating on M. californianus *Shells*

Each uncooked *M. californianus* shell contained outer calcite layers that appeared blue, with an outer brown periostracum (if not worn away in the intertidal zone). Parts of the calcite layer in many shells were abraded away by wave activity and contact with adjacent mussels, exposing the inner, nacreous aragonite layer of the shell (Fig. 4a). After a shell had been boiled or steamed for 30 minutes, it was identical in appearance to the uncooked shell (Fig. 4b). This amount of time would be more than adequate to cook the meat and allow the shell to open.

After heating a mussel shell in a furnace at 150ºC for 30 minutes, there was still minimal macroscopic change to the shell, and it still appeared the same as an uncooked shell (Fig. 4c). The first changes in the appearance of the shell occurred at 250ºC (Fig. 4d). After 30 minutes at this temperature, the shell lost its blue color and instead appeared light tan. The outer organic layer of the shell started to burn and turn black. However, despite this color change, the shell's integrity remained and it did not appear to have become more friable or to have cracked. At 350ºC there were clear changes in the structure of the shell (Fig. 4e). The organic coating became charred and

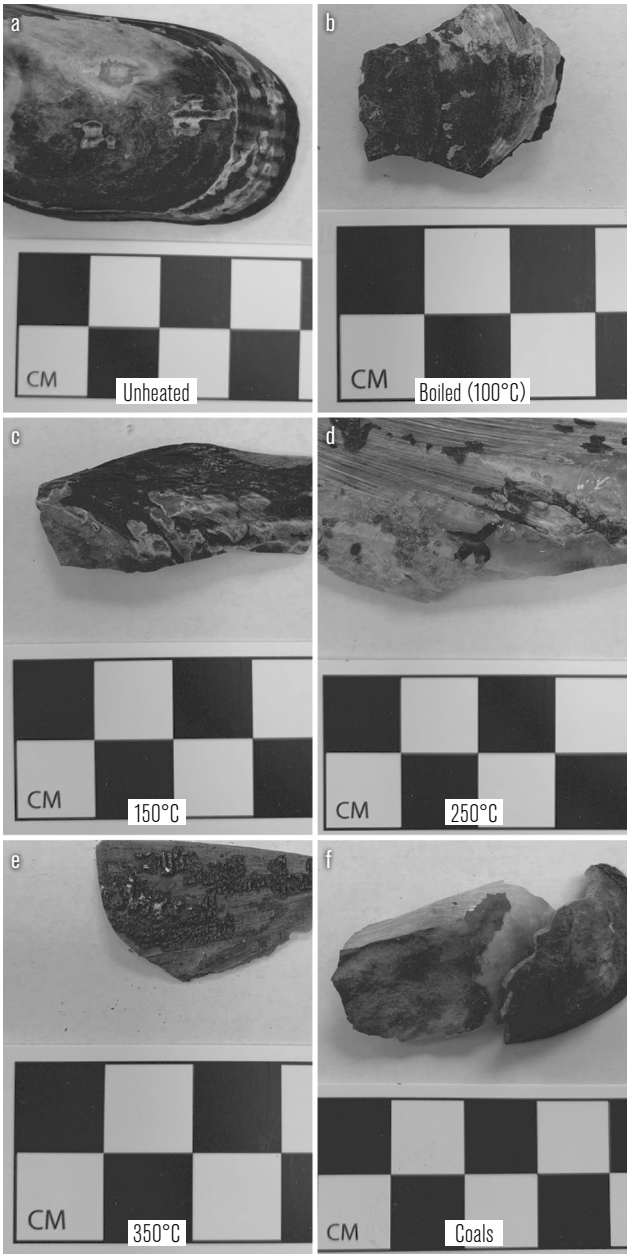

Figure 4. Macroscopic images of unheated and heated *M. californianus* shells: (a) unheated; (b) boiled for 30 min; (c) heated at 150ºC for 30 min; (d) heated at 250ºC for 30 min; (e) heated at 350ºC for 30 min; (f) heated on hot coals for 30 min. Note that the heated shells were broken into relatively flat pieces to they could be placed under a microscope.

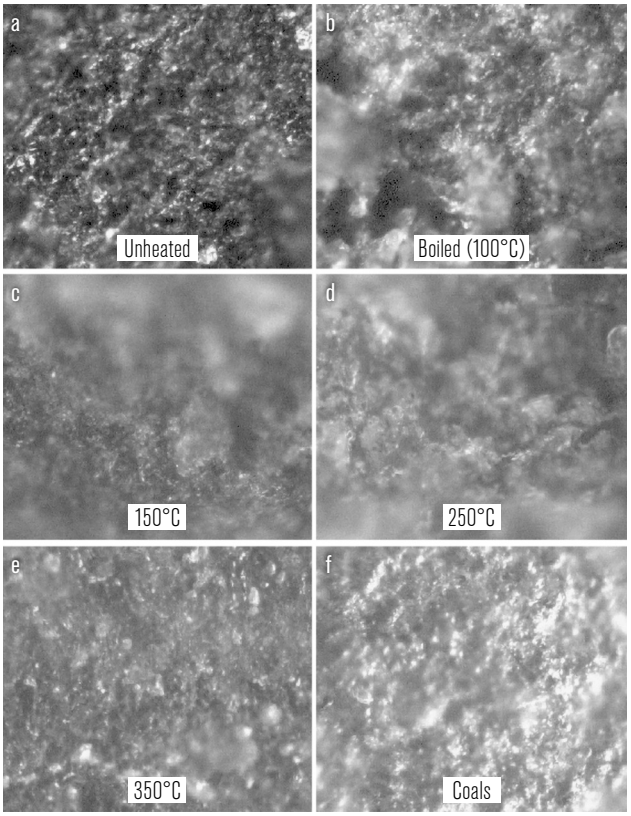

Figure 5. Microscopic images of unheated and heated M. californianus shells magnified at 20x: (a) unheated; (b) boiled for 30 min; (c) heated at 150ºC for 30 min; (d) heated at 250ºC for 30 min; (e) heated at 350ºC for 30 min; (f) heated on hot coals for 30 min. Note that the blurry sections of the images were caused by the difficulty of focusing on shells with natural undulations. Images (a), (b), and (c) are darker, reflecting their blue color, and images (d), (e), and (f) are lighter, reflecting their tan or smoky color.

the shell calcite darkened and started to become ashier. The shell cooked at 350ºC also became more friable and broke apart easily. The shell cooked on coals resembled the shell cooked at 350ºC, although it was less ashy and became friable (Fig. 4f). The shell color darkened but did not lose as much of the blue hue.

Unlike the macroscopic appearance of the shell, changes in the microscopic appearance of the shell surface were relatively minimal (Fig. 5). The most readily observable difference involves the color of the shell surface, with the boiled/steamed shell and the one heated at 150ºC retaining the blue color of the uncooked shell. The shells heated at 250ºC, 350ºC, and on coals are clearly lighter in color, appearing tanner. Nonetheless, the crystalline structure of the shell remained uniform during all cooking sessions, indicating that different methods did not cause a significant restructuring of the shell matrix.

Table 1

COMPILED ISOTOPIC DATA, WITH AVERAGE $\delta^{13}C$ AND $\delta^{18}O$ MEASUREMENTS BEFORE AND AFTER HEATING, AND THE DIFFERENCES BETWEEN THEM

Sample Type	Heating Method/ Temperature		$\delta^{13}C$			$\delta^{18}O$		
			Average	Standard Deviation	p-value	Average	Standard Deviation	p-value
Full Shell	Steamed	Before Heating	−0.07	0.40		−0.16	0.39	
		After Heating	−0.11	0.44		−0.21	0.41	
		Difference	−0.05	0.17	0.04	−0.05	0.19	0.22
Powder	Boiled	Before Heating	−0.03	0.28		−0.11	0.40	
		After Heating	0.01	0.28		−0.07	0.42	
		Difference	0.04	0.07	0.02	0.04	0.13	0.20
	150°C	Before Heating	0.42	0.33		−0.35	0.44	
		After Heating	0.52	0.31		−0.48	0.42	
		Difference	0.10	0.18	0.03	−0.13	0.13	0.00
	250°C	Before Heating	0.39	0.29		−0.20	0.25	
		After Heating	0.37	0.29		−0.35	0.21	
		Difference	−0.01	0.07	0.38	−0.15	0.15	0.00
	350°C	Before Heating	0.42	0.42		0.13	0.23	
		After Heating	0.28	0.46		−0.32	0.39	
		Difference	−0.14	0.14	0.00	−0.44	0.36	0.00
	Coals	Before Heating	0.14	0.23		−0.17	0.24	
		After Heating	−0.01	0.43		−0.30	0.42	
		Difference	−0.16	0.30	0.03	−0.12	0.30	0.09

P-values from paired two-tailed t-tests are listed for $\delta^{13}C$ and $\delta^{18}O$ for each heating method. Supplemental data are available upon request from the senior author.

The Effects on $\delta^{13}C$ and $\delta^{18}O$ of Heating Shells

Overall, as is often the case in similar analyses of shell carbonate, the data contain substantial noise, with differences between the measurements of samples involved in each heating method (Table 1). We plotted the $\delta^{13}C$ and $\delta^{18}O$ values for shell powder before and after cooking for all samples. Deviation from a 1:1 relationship between analogous samples before and after heating would indicate a change in isotopic composition, so we plotted this line along with a range for measurement error of 0.06‰ for both $\delta^{13}C$ and $\delta^{18}O$ (Fig. 6). Additionally, we conducted a paired two-tailed t-test in Microsoft Excel as a statistical assessment of whether $\delta^{13}C$ and $\delta^{18}O$ values were systematically altered by heating. Overall, there is a clear relationship between the effect of heating and the cooking method used.

Boiling/steaming does not appear to alter the isotopic values of the shell carbonate, with an average difference between the unheated and heated values of 0.04‰ for both $\delta^{13}C$ and $\delta^{18}O$. This is within the range of measurement error for both. All but one sample had a difference of 0.2‰ or less. P-values derived from the t-tests of these data are 0.02 for $\delta^{13}C$ and 0.20 for $\delta^{18}O$. The value for $\delta^{13}C$ is less than the threshold p-value of 0.05 often used to assess statistical significance, indicating that while there may have been a systematic change, it was small and within the range of instrument error. When considering shells that were steamed whole, there was no clear pattern in the difference between heated and unheated carbonate (Table 1; Fig. 7). The average differences were −0.05 for both $\delta^{13}C$ and $\delta^{18}O$, which is within the range of measurement error. P-values for the change in $\delta^{13}C$ and $\delta^{18}O$ are 0.04 and 0.22, respectively, following the same pattern present in the samples heated as powder. Interestingly, the changes in the powdered samples are both positive and in the steamed shells are both negative, indicating that they are more likely to be the product of instrument error than changes resulting from heating.

Heating the shells to 150ºC had a somewhat larger impact, with an average difference of 0.1‰ for $\delta^{13}C$ and −0.13‰ for $\delta^{18}O$. There are more extreme outliers at this temperature, with two shells increasing $\delta^{13}C$ by 0.64‰ (shell 1, 2 mm.) and 0.46‰ (shell 1, 12 mm.). The t-test

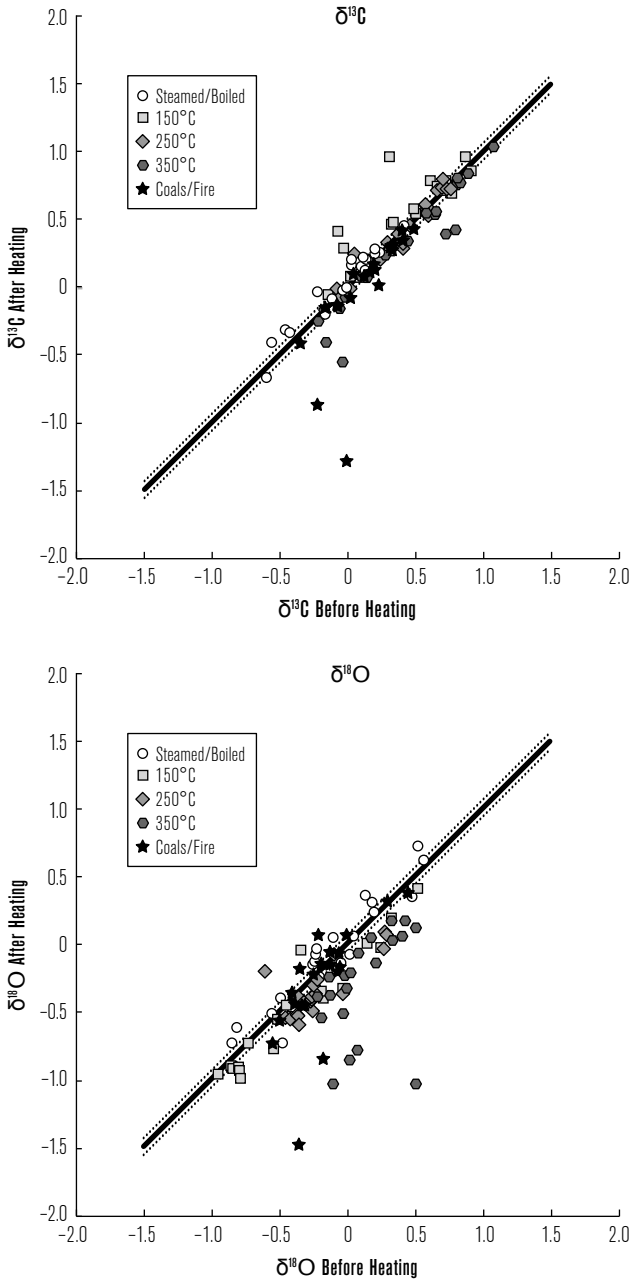

Figure 6. Isotopic ratios before and after heating for all shell powder samples. Data are presented as $\delta^{13}C$ and $\delta^{18}O$ after heating plotted against the same sample before heating, with the 1:1 line indicating no change along with dashed lines indicating measurement error overlaid on the plots.

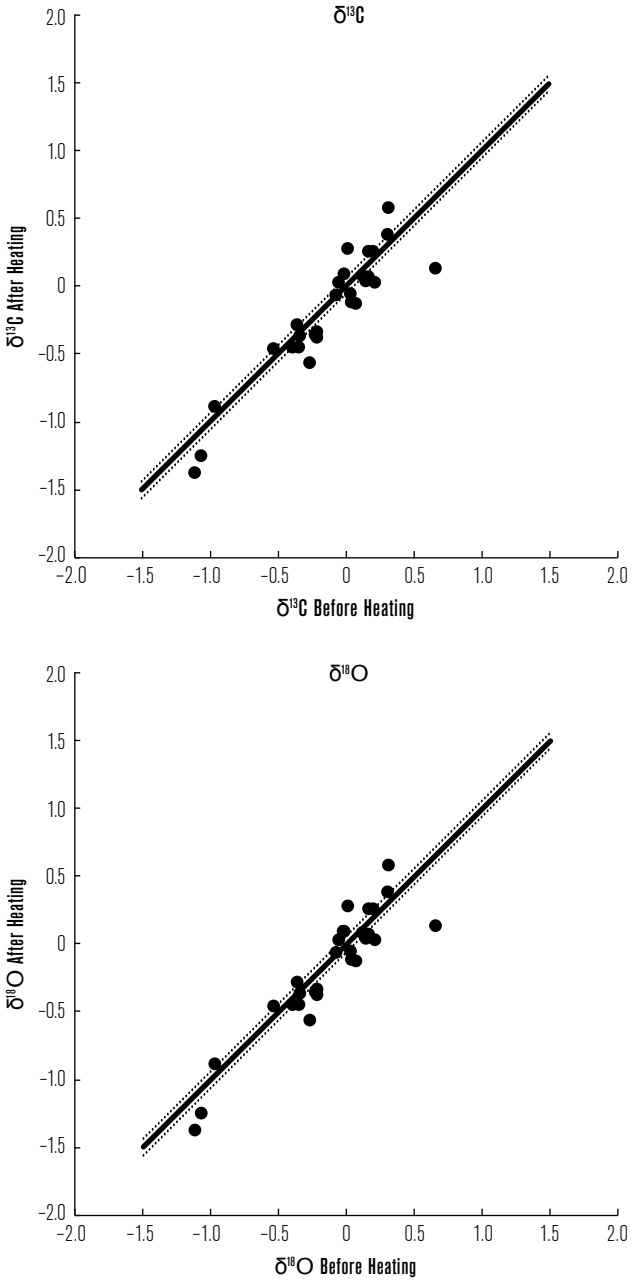

Figure 7. Isotopic ratios before and after heating for samples heated as whole shells. Data are presented as in Figure 6.

of $\delta^{13}C$ yields a p-value of 0.03 and of $\delta^{18}O$ a p-value of <0.01. This indicates a significant change in the $\delta^{18}O$ at this temperature. $\delta^{13}C$ is more difficult to assess, both because the change may be driven by outliers and because the trend toward more positive values is opposite the pattern observed for higher temperatures. In the macroscopic visual observations, the shells heated by steaming/boiling and at 150ºC do not show any change in color. This indicates that it is possible for a shell to have its $\delta^{18}O$ values altered without a visual change in the shell.

At 250ºC, the shell loses its blue color and appears tan. The average change in $\delta^{13}C$ was –0.01‰, within the range of instrument error, and there does not appear

to be a preference for an increase or decrease in the isotopic composition. This is supported by the t-test, which yielded a p-value of 0.38. $\delta^{18}O$, on the other hand, shows a preference for a small decrease upon cooking. Overall, 18 of the 20 shells experienced a decrease in $\delta^{18}O$ upon heating, with an average difference of −0.15‰. This is supported by a p-value of < 0.01. The largest differences in isotopic values occurred at 350ºC, where there is a systematic decrease in both $\delta^{13}C$ and $\delta^{18}O$ in all 20 samples. This difference is more pronounced for $\delta^{18}O$. The average difference in $\delta^{13}C$ at 350ºC is −0.14‰, indicating a relatively small change. For $\delta^{18}O$, the average difference for all 20 samples was −0.44‰, with a range from −0.15‰ to −1.57‰. In both contexts, the p-value derived from the t-test is < 0.01. Three shells underwent changes of, −1.57‰, −0.95‰, and −0.91‰, suggesting that extreme heat may have large effects on the $\delta^{18}O$ values of the shell carbonate.

Despite the fact that shells placed on coals also show macroscopic changes to the shell, the $\delta^{13}C$ and $\delta^{18}O$ values do not experience as large a change upon heating as occurred in those cooked in the furnace. The overall average change in $\delta^{13}C$ was −0.16‰ and in $\delta^{18}O$ was −0.12‰. The t-test yields p-values of 0.03 for $\delta^{13}C$ and 0.09 for $\delta^{18}O$. Two shells experienced a large change in both isotopic values. Shell 7, 2 mm. from the edge, had a change in $\delta^{13}C$ of −0.66‰ and in $\delta^{18}O$ of −0.70‰, and shell 8, 4 mm. from the edge, had a change in $\delta^{13}C$ of −1.3‰ and in $\delta^{18}O$ of −1.14‰. If these are disregarded, the average change in $\delta^{13}C$ is −0.07‰ and in $\delta^{18}O$ is −0.03‰. The latter is within the range of instrument error. This high amount of variability could be a result of the uneven heating of the shell powder samples, and therefore heating on coals may only alter those shells or the parts of shells close to the fire or touching wood that is actively burning.

DISCUSSION

Our experimental study suggests that in some contexts, heating can alter the $\delta^{13}C$ and/or $\delta^{18}O$ composition of *M. californianus* shell carbonate in the outer calcite layer, which is frequently sampled for paleoenvironmental and season of harvest studies (e.g., Glassow et al. 1994; Jazwa et al. 2012, 2015; Jew et al. 2013a, 2013b; Thakar 2014). Owing largely to their abundance in many intertidal zones along the Pacific Coast of North America, *M. californianus* frequently comprises the major contributor to shell midden sites in California. For this reason, it is the most frequent target for archaeologists conducting isotopic tests. Because mussels are cooked to open the shell, it is necessary to understand the response of a shell's isotopic composition to different methods of heating. The two most common methods of cooking shells described in the ethnographic literature in California are boiling and roasting (Gifford 1939; Jones and Richman 1995; Kroeber and Barrett 1960). Our study indicates that boiling or steaming shells does not alter their appearance, structure, or isotopic composition. Roasting shells over coals, however, alters the color of the shell, causing it to lose much of its blue color, and possibly become more friable. Shells heated on coals are subject to varying temperatures based on their position relative to the fire. Only when the shells are subjected to especially high temperatures (i.e., are burned either intentionally or unintentionally) do they experience a systematic change in isotopic composition, which manifests itself as a decrease in both $\delta^{13}C$ and $\delta^{18}O$ values.

When performing a similar experiment involving fish otoliths, Andrus and Crowe (2002) observed a decrease in $\delta^{13}C$ and $\delta^{18}O$ values when the fish were burned on hardwood coals for ~6 hours at approximately 200ºC, but no change occurred during any other form of cooking. This decrease was substantially larger than we observed, with a decrease of roughly 1.5‰ and 3‰ for $\delta^{18}O$ and roughly 3.5‰ and 8‰ for $\delta^{13}C$. They did not subject their samples to temperatures as high as we did, so it is unclear how that may have affected the isotopic composition of the otoliths. Andrus and Crowe (2002) speculate that these isotopic changes may have occurred during the displacive polymorphic reaction of aragonite to calcite. Despite the fact that this reaction should not change the isotopic content, since it only involves a restructuring of the crystal lattice, they suggest that isotopic exchange may have occurred between atmospheric CO_2 and H_2O and carbonate during inversion (citing Epstein et al. 1953), possibly leading to this change. Milano et al. (2016) subjected *Phorcus turbinatus* shells to temperatures as high as 700ºC, also observing decreases in $\delta^{18}O$ values as high as 3.3‰. The carbonate in this species was also in the form of aragonite, which experienced a partial change to calcite during the experiment.

In our experiment, we tested carbonate from the outer shell of *M. californianus*, which is calcite, so a similar transition would not have taken place. The inner layer of the shell is made of aragonite, but we were careful to sample only the calcite layers. It is possible that we inadvertently included aragonite in some of our samples, but it is less likely that we did so systematically for most or all of the shells. We speculate that under high temperatures, a similar exchange of CO_2 and/or H_2O with the atmosphere may occur. If the process were as simple as water evaporating from the shell, we would expect the water that was lost to include oxygen that was preferentially light (i.e., involving more ^{16}O) and the remaining carbonate should be enriched in ^{18}O. Conversely, and consistent with previous studies, we observed a decrease in $\delta^{18}O$, suggesting that the process is more complicated than this.

Implications for Paleoenvironmental and Archaeological Studies

While this experiment has interesting implications for understanding shell dynamics under different heating regimes, our results have especially practical implications for paleoenvironmental and archaeological analyses that rely on *M. californianus* and other mollusk shells. The use of zooarchaeological materials to understand past environments is especially powerful because it directly ties the chronology of patterns of natural change to that of human settlement, subsistence, and other activities. Rather than reconciling samples from different timelines, we know that the environment during the shell's lifetime was what the person who consumed its meat experienced. The fact that a human likely heated the shell before removing its meat adds an additional complicating factor that would not exist when dealing with the shell of a mussel that had died naturally and was not heated.

While the use of $\delta^{18}O$ to reconstruct past SST remains a powerful tool, our study shows that it is important to consider the effects of heating on the isotopic composition of shell carbonate, even if it is calcite. We expect that those shells in the archaeological record that were boiled or steamed should be visually indistinguishable from uncooked shells, but it also appears that cooking the shells in this way would not have affected their isotopic composition anyway. When shells that were cooked in a furnace at a relatively low temperature (150ºC) were examined—and which also appeared macroscopically and microscopically identical to uncooked shells—there was a systematic but small decrease in $\delta^{18}O$. When *M. californianus* shells retain their characteristic deep blue color, it is likely safer to sample carbonate for analysis, and any changes present are probably small.

This experiment also indicates that in most cases involving shells that were roasted on coals, the heat's effects on the $\delta^{13}C$ and $\delta^{18}O$ of the shell are variable and difficult to predict. When shells are exposed to extreme heat, as in those closest to the fire, their isotopic values may become reduced. When three whole shells were heated on the campfire at the same time as the shell powder, one of the three shells caught on fire and acquired a very distinct appearance from the other two. The shell turned a grayish color and became especially friable. While analyzing midden deposits from sites on Santa Rosa Island, we have observed shells that were clearly burned in this way, but they are relatively uncommon. Instead, most shells, while highly fragmented, do not exhibit signs of burning.

While we have provided evidence that high temperatures outside the range typically encountered when shells are boiled or roasted do appear to alter the shells' isotopic composition, an important question is what the practical implications of this might be for paleoenvironmental reconstructions. Here, we use the equation for estimating SST from Horibe and Oba (1972):

$$t^{o} = 17.04 - 4.34(\delta c - \delta w) + 0.16(\delta c - \delta w)^2 \qquad (1)$$

This equation was modified from the original by Epstein et al. (1953). Here δc is the measured $\delta^{18}O$ value from the sample and we use an island-wide average of −0.26‰ for δw, the $\delta^{18}O$ of ambient seawater (Jazwa et al. 2015). The average values of $\delta^{18}O$ for powder heated at 350ºC are 0.13‰ before and −0.32‰ after. This yields a change in the SST estimate from 15.4ºC to 17.3ºC. While the annual range in SST can vary through time, a 15-day running average of SST variation between April 1981 and December 1992 from a buoy near Santa Rosa Island indicates that the typical annual variation is approximately 5ºC for this smoothed curve, but the full range of variability can be as high as 10ºC (Jazwa et al. 2015). Therefore, an increase in the estimated SST of between 2ºC and 4ºC can alter our interpretations about past climate.

Furthermore, the amount that $\delta^{18}O$ values decrease under high heat does not appear to be systematic, and this variability is only compounded when cooking on coals, since different parts of the shell may be exposed to different amounts of heat. If all of the isotopic values shifted uniformly and predictably, it would still be possible to estimate season of harvest for the shell and to make inferences about the season of occupation for the site as a whole, even if the estimated SST values were not correct. However, the variability in isotopic values would likely preclude a confident determination of the season of harvest in cases in which the shell was subjected to high temperatures. For these reasons, we suggest that whenever possible, tests should be performed on shells that maintain their blue color and appear to be uncooked.

CONCLUSIONS

In this experimental study, we assess the effects of heating on the oxygen and carbon stable isotopic composition of *M. californianus* shells from Santa Rosa Island, California. Early studies focused on the utility of estimating SST from the $\delta^{18}O$ in shell carbonate (e.g., Epstein et al. 1951, 1953; Horibe and Oba 1972). More recently, work has been done to refine methods for estimating the season of harvest for individual shells and making inferences about the season of occupation of archaeological sites (e.g., Culleton et al. 2009; Jazwa and Kennett 2016; Jew et al. 2013a, 2013b; Shackleton 1973). Here, we expand the study of isotope dynamics to assess the role of anthropogenic alterations of shell calcite to determine when caution should be used in selecting shells for analysis and interpreting data from suspect shells. Put simply, we recommend that preference should be given to those shells that retain their natural blue color and do not appear to have been burned. Still, it is only when shells are exposed to extreme heat—which is not typically encountered during boiling, steaming, or roasting—that we expect to see isotopic changes that can influence our interpretations about SST or seasonality.

While isotope geochemistry has become more common in the archaeological literature, it is important to consider limitations to these methods. This simple experimental study was focused on a single anthropogenic impact—heating—on a single species of mollusk, *M. californianus*. Additional studies should be performed to understand the effects of similar processes on other species that might have different shell chemistries or structures. Other natural or anthropogenic impacts on shell composition should also be considered. By doing so, it will increase the applicability and accuracy of these powerful techniques that have great potential to help us understand the human past.

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