Ba/Ca variations in the modern intertidal bean clam *Donax gouldii*: An upwelling proxy?

Marco B.A. Hatch a,⁎, Stephen A. Schellenberg b, Melissa L. Carter a

a Scripps Institution of Oceanography, University of California, San Diego, La Jolla, CA 92093-0208, USA
b Department of Geological Sciences, San Diego State University, San Diego, CA 92182-1020, USA

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ABSTRACT

The discovery and calibration of high resolution paleoceanographic proxies is necessary to extend historic climate records and to understand regional climate variability. Chemical variations of skeletal remains have emerged as an often reliable recorder of environmental conditions. Specifically, Ba/Ca ratios have been correlated to temperature, salinity, seawater Ba/Ca, and phytoplankton biomass, although, many of these relationships appear taxon- and location-specific. To assess the sub-weekly Ba/Ca variations in the intertidal shallow-burrowing bivalve *Donax gouldii*, specimens were collected from the Southern California Bight, skeletal growth increments were cross-dated based on tidal-driven growth patterns, and skeletal aragonite Ba/Ca was determined using laser ablation inductively coupled plasma mass spectrometry. Cross-dated growth among specimens revealed a simultaneous, large, and transient Ba/Ca peak in all shells. The timing of peak Ba/Ca was compared to a suite of locally measured physical and biological data, including temperature, salinity, density, nitrate, silicate, chlorophyll, diatom abundance, dinoflagellate abundance, and phytoplankton community composition. Based on cross-dated chronologies, Ba/Ca peak is significantly correlated with Chl a from six to nine days prior and nutrients (nitrate, phosphate, silicate, and nitrite) from three days prior. In this system diatom abundance was not related to Ba/Ca peak. Transiently higher seawater Ba/Ca resulting from upwelling may be reflected in peak Ba/Ca, however the exact mechanisms leading to population wide Ba/Ca peaks remains enigmatic.

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1. Introduction

Phytoplankton primary productivity supports a diverse array of marine ecosystems and sustains an important global carbon flux from the atmosphere into the deep ocean through the export production of organic matter (Behrenfeld et al., 2006). As anthropogenic global warming and ocean acidification progressively alter the global ocean system, scientific and policy communities would benefit from a more dynamic understanding of the myriad controls on primary productivity over both time and space (Sarmiento et al., 1998). One avenue for improving this understanding is the reconstruction of spatiotemporal variations during prehistoric climate regimes, and the comparison of such “proxy-based” data to computational models (Jones et al., 2001).

The concentration of barium (Ba) in seawater, marine sediments, and biogenic carbonates has long generated interest in the element’s potential as a proxy for upwelling and thereby indirectly primary productivity (Bacon and Edmond, 1972; Lea and Boyle, 1989, 1991; Shaw et al., 1998). In the ocean, Ba typically displays a nutrient-type distribution with low concentrations in the mixed layer and increasing concentrations with depth due to remineralization and respiration (Chan et al., 1977). Higher bulk sediment Ba concentrations are common under regions of higher primary productivity (Goldberg and Arhenius, 1958; Bacon and Edmond, 1972; Dehairs et al., 1980), and have been attributed to adsorption of dissolved barium onto iron oxyhydroxide substrates associated with diatom frustules (Sternberg et al., 2005) and direct precipitation of barite (Momin et al., 1999). The flux of barite is not constant with depth and accumulates at mesopelagic depths, particularly under areas of high productivity (Dehairs et al., 1987, 1992). Higher Ba/Ca ratios within biogenic carbonate skeletons also correspond with higher seawater Ba concentrations; for example, elevated Ba/Ca is measured in the calcitic tests of planktonic foraminifera (Lea and Boyle, 1989) and the aragonitic skeletal layers of scleractinian corals when deeper Ba-rich water is upwelled (Lea et al., 1989; Allibert and Kinsley, 2008).

In bivalves, Ba/Cashell ratios along shell growth profiles are typically relatively low (i.e., <10 μmol/mol), and many contain population wide synchronous peaks (Stecher et al., 1996; Vander Putten et al., 2000; Gillikin et al., 2006; Barats et al., 2007; Gillikin et al., 2008; Barats et al., 2009; Thébault et al., 2009). Background Ba/Cashell is broadly consistent with ambient seawater Ba concentrations with a Ba seawater–shell partition coefficients of 0.07–0.18 for both calcite

⁎ Corresponding author.
E-mail address: marco.hatch@gmail.com (M.B.A. Hatch).

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and aragonite (Gillikin et al., 2006, 2008). In the aragonitic Saxidomus giganteus, ten years of continuous Ba/Ca_{shell} show remarkably synchronous inter-individual variability, suggesting that Ba/Ca_{shell} is related to some environmental parameter (Gillikin et al., 2008). A common working hypothesis, first proposed by Stecher et al. (1996), attributes such peaks to increased ingestion of Ba-rich phytoplankton (e.g., diatoms (Sternberg et al., 2005)) or suspended barite precipitates with subsequent internal transport via the hemolymph into the extrapallial fluid and thereby the shell structure. This diatom-diet-based hypotheses is supported by Vander Putten et al. (2000), who argued for a positive correlation between ambient chlorophyll a (Chl a) and Ba/Ca_{shell} in the temperate North Atlantic mussel Mytilus edulis, and by Thébault et al. (2009), who demonstrated a significant positive correlation between ambient Chl a and Ba/Ca_{shell} in the tropical New Caledonian scallop Comptomallium radula. Importantly, both studies assumed that gross Chl a concentrations were a sufficient proxy for the often complex variability in phytoplankton biomass and diversity— an assumption that can be problematic given that Chl a concentrations do not offer taxonomic identification, vary widely between phytoplankton species and are influenced within species by ambient environmental conditions such as light, temperature, and nutrients ( Mullin et al., 1966; Chan, 1980; Cullen, 1982; Geider, 1987). In contrast, Gillikin et al. (2008) found no relationship between Chl a and Ba/Ca_{shell} in the temperate North Atlantic scallop Pecten maximus.

If Ba/Ca_{shell} does reliably record environmental conditions (e.g., diatom blooms, upwelling), then historic (e.g., museum, archaeological, and geological) shells could be exploited to characterize the frequency with which phytoplankton blooms occur and their constituent taxa. Previous studies have been limited in their ability to precisely date bivalve growth increments (i.e., to quasi-daily-resolution) suffering from uncertainties associated with growth increment back-counting (e.g., missed increments due to growth shutdown, false increments due to disturbance) (Thébault et al., 2009). Such dating errors can be greatly reduced, if not avoided, by utilizing the dendrochronology method of cross-dating, which aligns individual growth increments within and among specimens in the time-domain. Cross-dating, in combination with high sampling resolution via laser ablation techniques and sufficient ambient environmental monitoring of nutrient concentrations and phytoplankton dynamics could provide important constraints on the potential environmental causes of Ba/Ca_{shell} peaks.

The aim of the study is to assess relationships between sub-weekly-to-daily variations in monitored environmental conditions (i.e., phytoplankton dynamics, nutrient measurements, temperature and salinity variations) and Ba/Ca variation in cross-dated D. gouldii shells via laser ablation inductively coupled plasma mass spectrometry (LA-ICP-MS). D. gouldii is a relatively small (<25 mm) and short-lived (<3 years) aragonitic bivalve that inhabits the swash zone of sandy open coast beaches from Point Conception, California to Acapulco, Mexico (Coe, 1955). This species is an ideal candidate for cross-dating given its distinct sub-annual growth increments. D. gouldii shells are common in late Holocene Native American middens (Gallegos, 2002) as well as wave-cut terrace deposits from oxygen isotope stages 5a (~85 ka) and 5e (~125 ka) (Valentine, 1960; Gallegos, 2002).

2. Methods

2.1. Location and oceanographic context

The Southern California Bight is characterized as a seasonally stratified oceanographic regime wherein wind-driven upwelling provides dissolved nutrients to the mixed layer. Along the shallow coastal waters off of the Scripps Institution of Oceanography (SIO) (Fig. 1A), regional wind-driven upwelling indices are poorly correlated with local chlorophyll a (Chl a), sea surface temperature (SST), and sea surface salinity (SSS). In addition, local phytoplankton blooms are significantly correlated in timing, but not magnitude, to phytoplankton blooms at the nearest California Cooperative Fisheries Investigation station (CalCOFI station 93.27; 18 km offshore). However, local blooms are not correlated to the CalCOFI stations farther offshore or to regional upwelling indices (Kim et al., 2009). Based on these observations, Kim et al. (2009) proposed that local dissolved nutrient delivery, and thereby local productivity, were less related to regional wind-driven upwelling and more related to a combination of internal waves, longshore transport, and cross-shore transport. Given the lack of correlation with offshore stations, we chose to focus on local records of ambient environmental conditions from the SIO Pier rather than using offshore buoy- or satellite-derived data.

2.2. Temperature and salinity time-series

Temperature and salinity samples were taken daily from sea surface and five meters water depth at SIO Pier as part of the Shore Station Program (http://shorestation.ucsd.edu). Temperature was measured by immersing a calibrated thermometer in a bucket sample and reading to 0.1 °C. Salinity was determined from a Guildline inductive salinometer (Model 8410) using the algorithms for the 1979 Practical Salinity Scale (UNESCO, 1981). SIO Pier five meter salinity and temperature data were used to calculate seawater density (σt).

2.3. Chlorophyll, nutrients and phytoplankton cell counts

Sea surface water samples for Chl a and nutrients were collected twice per week (typically Monday and Thursday) and weekly phytoplankton cell counts were done at the SIO pier as part of the Southern California Coastal Ocean Observing System, Harmful Algal Bloom Monitoring Program (http://www.sccoos.org/data/chlorophyll/index.php). Chl a values were obtained using standard chlorophyll extraction and analysis procedures outlined by (Venrick and Hayward, 1984) in which seawater was filtered using a ~0.7 μm glass fiber filter and photosynthetic pigments were extracted by soaking in 10 mL of 90% acetone for 24 h before concentration was determined on a calibrated Turner

10 AU fluorometer. Dissolved nutrient concentrations were collected using acid-washed plastic containers and were filtered through 0.7 glass fiber filters to remove particulates before being stored frozen at −20 °C. Nutrient analyses (phosphate, silicate + nitrite, nitrite, and ammonia) were performed on a Seal Analytical continuous-flow AutoAnalyzer 3 (AA3) following standard methods (Armstrong et al., 1967; Atlas et al., 1971; Hager et al., 1972; Gordon et al., 1992). Abundance of all diatoms and dinoflagellates greater than 5 μm in diameter and other specific taxa related to the harmful algal bloom program (e.g., Lingulodinium polyedrum, Gymnodinium spp., Pseudo-nitzchia spp.) were determined from settling 10–50 ml of seawater preserved with 4% formaldehyde (Utermöhl, 1958; UNESCO, 1981). Cells were identified and tallied to the lowest feasible taxonomic level through a phase-contrast, inverted light microscope at 200×. Sample volume varied between 1.25 ml and 25 ml (1/8 to 1/2 of slide) and detectable cell abundance was between 80 and 800 cells/L, depending on cell size. To increase overlap with the cross-dated Ba/Ca shell data, each nutrient measurement, Chl a measurement, and phytoplankton count were assumed to be representative of the day before and after their specific collection.

2.4. Specimens collection and preparation

D. gouldii were collected from the sandy shoreline of the Scripps Coastal Reserve within 100 m from the SIO Pier during lower low tides (e.g., <0.2 m Mean Lower Low Water (MLLW)) from February 2008 to July 2008 (Fig. 1A). Unlike other species of this genus, D. gouldii does not markedly migrate with the tidal level, but is consistently most densely distributed between 0.3 and 0.1 m MLLW (Haderlie and Abbott, 1980; Ellers, 1995). Specimens from the following dates were selected for cross-dating: 22 February (n=2), 23 March (n=3), 14 April (n=2), 21 May (n=2), 9 June (n=2), and 8 July (n=8). For each specimen, one valve was thin sectioned by embedding in epoxy (Fig. 1B), cut along the maximum growth axis with a Buehler Isomet 5000 Linear Precision Saw, and hand-polished with 3M Wet or Dry Sandpaper (320, 600, 800, and 1000 grit) using a duct-tape manipulator (Carpenter, 1998) to a final thickness of ~100 μm. Four additional specimens were selected from the 8 July collection were thin sectioned to final thickness of ~800 μm for laser ablation.

For digital growth increment measurement, shells were imaged with a Paxcam digital microscope camera (http://www.paxcam.com/) attached to a Leica MZ16 microscope using transmitted-light dark-field illumination at 50× magnification producing 10–20 images per shell. Images were manually mosaiced into a single image using Adobe Photoshop CS (http://www.adobe.com/). Under these conditions, growth increments within D. gouldii are characterized by thin (~6 μm) and light (more transparent) regions bounded by thicker (~30 μm) and darker (more opaque) regions (Fig. 2).

2.5. Cross-dating

Cross-dating ordinates discrete growth increments within and among specimens into a common time-domain. The method is based on the presumption that ambient environmental variability will produce a common and congruent growth-increment pattern among contemporaneous specimens (Yamaguchi, 1991; Black et al., 2005, 2008). For example, at an annual scale, an environmentally favorable year would result in a relatively wide annual growth increment, whereas an environmentally unfavorable year would result in a relatively narrow annual growth increment. Cross-dating utilizes such environmental-induced variation in growth increment widths to align individual samples’ time-series of growth-increment widths into a common time-series for the broader population. Individual growth-increment time-series can be incorrectly documented by including false growth increments (e.g., those related to isolated disturbance) or by missing true, but faint, growth increments. Cross-dating effectively identifies such errors as deviations from the population-level growth-increment time-series. Thus, spurious “missing” or “extra” growth increments within an individual can be identified and corrected based on their deviation from prevalent growth-increment pattern. Cross-dating is routinely applied to annual growth increments of trees, rockfish, and long-lived bivalves (Black et al., 2009), and is applied here to growth increments with fortnightly to lunar day periodicity. This study cross-dated Donax specimens using two methods: (1) a variation of the traditional “list-year” method and (2) statistical quantification of growth-increment time-series congruence using standard dendrochronology methods.

In species with annual growth increments, the “list-year” method requires the initial identification of growth increments which are anomalously wide or narrow and shared among the sample population. These anomalous annual growth increments are then dated by back-counting of annual growth increments from the growth-margin back to the anomalous annual growth increment. If dating of anomalous growth increments is consistent among specimens, then the working hypothesis that these anomalous annual growth-intervals are synchronous among specimens is supported. For an overview of this method as applied to bivalves, see (Black et al., 2008).

For D. gouldii, this “list-year” method was modified into a “list-lunar-day” method and applied to randomly selected specimens from each collection date. In thin section, D. gouldii shells consisted of intervals of pronounced bundles (PB) of distinct growth increments separated by intervals of poorly resolved growth increments (Fig. 2). These alternations limited assignment of lunar dates by back-counting to the PB immediately adjacent to the shell commissure. For a given collection date, the number of growth increments within the commissure adjacent PB was constant. For example, within their respective commissure-adjacent PBs, all specimens from 21 May consistently contained three growth increments (Fig. 3A–B). Based on these consistent patterns, inner PBs in specimens from later collection dates were matched to commissure-adjacent PBs from earlier collections, which then allowed lunar day assignment to each distinct growth increment within each PB within each specimen (Fig. 3).

To quantitatively test cross-dating, a continuous string of growth-increment widths was created by digitally marking each clear growth increment starting from the commissure and working toward the
umbo. The resulting growth-increment string consisted of numbered growth increment widths, with sections of poorly resolved growth between each pair of PBs being treated as a single growth increment. Growth increments were marked at the growing edge and measured using the ObjectJ plugin (Vischer, 2011) for ImageJ (Rashband, 1997–2011). Cross-dating was statistically verified using the dendrochronology program COFECHA (available from the International Tree-Ring Data Bank Dendrochronology Program Library; http://www.ltrr.arizona.edu/software.html). The COFECHA program first detrends each chronology to remove ontogenetic effects using a cubic spline with a 50% frequency response of 32 increments. COFECHA then correlates each numbered growth-increment width to the average width for that growth-increment number with low correlations indicating potential cross-dating errors. Finally, the overall agreement of all chronologies is statistically quantified and expressed as a series intercorrelation value, which measures the relative strength of a common signal among all chronologies. The series intercorrelation has been shown to be highly sensitive to dating errors (Black et al., 2008). Once final chronologies had been determined, lunar dates were assigned to each distinct growth increment using methods analogous to those for the “list-lunar-day” cross-dating. Then dating was compared between the both cross-dating methods to verify dating congruence. Finally, lunar days were converted to calendar day by defining a lunar day as 24.8 h.

2.6. Laser ablation for Ba/Ca determination

Ba/Ca variations along the growth profile of four Donax gouldii specimens selected from the same age class collected on 8 July 2008 were determined using a New Wave UP-213 laser ablation system coupled to a Finnigan MAT Element 2 Sector Inductively Coupled Plasma Mass Spectrometer (ICP-MS) at the University of California, Santa Barbara. Ablation paths followed the central portion of observable growth increments within the prismatic layer, from the umbo to the commissure, and were spaced every 300 μm from anterior to posterior for specimens A and B and every 900 μm for specimens C and D. D. gouldii shells measured 17.1, 21.8, 18.2, 19.2 mm from anterior to posterior for specimens A, B, C, and D, respectively. All ablations were continuous scans, covering 100 μm using a 70 μm spot, taken parallel to growth increments, representing roughly one lunar day of biomineralization. Nuclide concentrations were calibrated against a carbonate-optimized in-house liquid standard for Ba/Ca (342.0 μmol/mol ± 3.4 (1.0% RSD)) (Zacherl et al., 2003). A solid glass (NIST 612) and carbonate (USGS MACS3) standard reference materials were run periodically to check analytical precision or repeatability. Average relative standard deviation for Ba/Ca (n = 24) was 6.6% (129.0 μmol/mol ± 8.5) for NIST 612 and 8.5% (47.6 μmol/mol ± 4.1) for USGS MACS3. The laser was operated at a repetition rate of 10 Hz with an RF power of 1200 W. The nebulizer flow rate of argon was 0.8 L min⁻¹ and 0.5 ml min⁻¹ through the sample chamber.

2.7. Statistical analysis

To increase temporal matches of the weekly to bi-weekly environmental data with the cross-dated Ba/Ca_Ashell data, each environmental datum was assumed to also be representative of the day before and after its specific collection date. In addition, because some temporal lag between environmental conditions and shell chemistry is reasonable and expected based on physiological principles (e.g., for the diet-based Ba/Ca causal mechanism of Stecher et al. (1996)) the dependent Ba/Ca variable was compared to each independent environmental variable from the same date as Ba/Ca_Ashell, three days prior, six days prior, and nine days prior using Pearson Product Moment Correlation Coefficients (PPMCCs).

3. Results

3.1. Cross-dating

Cross-dating was successfully applied to six D. gouldii specimens from the 8 July 2008 collection date, resulting in a series intercorrelation value of 0.937 based on the intercomparison of 299 growth increments. This chronology contained nine distinct PBs that contained between four and nine growth increments. The final master cross-dated chronology comprised of all specimens (22 February (n = 2), 23 March (n = 3), 14 April (n = 2), 21 May (n = 2), 9 June (n = 2), and 8 July (n = 8)) had a series intercorrelation of 0.845 based on 702 growth increments.

Using this master cross-dated chronology, the 75 laser ablations for the four specimens from the 8 July 2008 collection were ordinated in the time-domain by referencing the nearest resolvable growth increment or, if the ablation was located within a region of poorly-defined growth increments (i.e., neap tide conditions), by assuming...
a constant daily growth rate between the dated growth increments of the adjacent PBs.

3.2. Shell geochemistry

Ba/Cashell from 75 laser ablations for the four specimens ranged from 2.0 to 11.3 μmol mol⁻¹ with a mean of 3.9 μmol mol⁻¹ (±1.7). Based on cross-dating, six of the eight peak values (defined as >1 SD above the mean) occurred between 28 March 2008 and 3 April 2008 with values ranging from 6.4 to 11.3 μmol mol⁻¹ (Fig. 4A). The other two peak Ba/Ca values occurred on 21 May and 1 June with values of 7.5 and 5.7 μmol mol⁻¹, respectively. Pre-peak (11 February–27 March) values averaged 3.6 (±0.7) μmol mol⁻¹, while post-peak (4 April–8 July) values averaged 3.5 (±1.2) μmol mol⁻¹ and are more variable. These 75 Ba/Ca determinations cover 147 days of biomineralization (2/11-7/8) averaging one measurement every two days.

3.3. Physical and biological environment

During the study interval, SST varied from 13.2 to 23.7 °C and SSS was relatively constant with a mean of 33.69 PSU (±0.15) (Fig. 4B). Seawater density (σT) averaged 24.56 and varied from 22.80 to 25.64 (Fig. 4C). Nitrate and silicate both showed a transient peak on 27 March 2008 of 8.83 and 10.65 μmol/L, respectively (Fig. 5D). Seawater density (σT) at five meters was 25.14 on 27 March, the same date increased nitrate was observed, and values of >25.1 are associated with increased levels of nitrate (Parnell et al., 2010). The extended Redfield ratio of nitrate:silicate is roughly 1:1, suggesting that these nutrients were recently brought to the surface mixed layer (Dugdale and Wilkerson, 1998).

The dinoflagellate, *Lingulodinium polyedrum*, reached peak abundance on 17 March 2008 (80.6×10³ cells/L) and was responsible for the majority of the aforementioned Chl a peak (Fig. 5B). The increase in *L. polyedrum* is also seen in the total count of dinoflagellates, which peaks between 3 March 2008 (136.8×10³ cells/L) and 24 March 2008 (134.4×10³ cells/L) (Fig. 5B and C) with an average of 7.3×10⁴ cells/L. A second increase in dinoflagellates occurred on 28 April and 12 May 2008, however, *L. polyedrum* remained low (Fig. 5C).

Total diatoms averaged 5.1×10⁴ cells/L and peaked three times through the study interval, with a relatively small peak on 31 March 2008 (61.0×10⁴ cells/L), a larger peak on 5 May 2008 (21.1×10⁵ cells/L), and the largest peak on 2 June 2008 (22.1×10⁵ cells/L). The chain-forming diatoms *Chaetoceros* spp. and *Leptocylindrus* spp. visually dominated the 31 March and 5 May peaks (Carter, pers. Ob.) and the 2 June peak was dominated by small, narrow cells of *Pseudo-nitzschia* spp. (delicatissima group, frustule width <3 μm, length <50 μm) (Fig. 5C).

Chl a varied from 1.5 to 11.6 mg m⁻² with the highest value on 17 March 2008 followed by a steady decline to 3.4 mg m⁻² on 3 April 2008 (Fig. 5B). Chl a had a second smaller peak on 28 April of 7.2 mg m⁻². Over the entire study interval, Chl a and dinoflagellates were strongly correlated (*r² = 0.72, p < 0.0001*), whereas Chl a was weakly correlated with diatoms (*r² = 0.07, p = 0.29*) and total cell count (*r² = 0.15, p = 0.11*).

3.4. Correlations between environmental variables to Ba/Cashell

The Pearson Product Moment Correlation Coefficients (PPMCCs) method was used to test correlations between Ba/Cashell and fifteen environmental variables from the same day as Ba/Cashell, three days prior, six days prior and nine days prior (Table 1). Of the sixty correlations performed, the six found to be significant (p < 0.01) are nitrate, nitrite phosphate, silicate from three days prior and Chl a from six and nine days prior (Table 1).

4. Discussion

4.1. Cross-dating

Dendrochronology methods designed to date annual growth increments are here successfully modified and applied to lunar day
growth increments. The resulting master cross-dated chronology created from 29 specimens collected between 22 February and 8 July 2008 including 702 growth increments had a series intercorrelation value of 0.845. Although a standard threshold value to assess the strength of series intercorrelation values has not been established, values greater than 0.70 are considered high and have been observed in other bivalves (Black et al., 2008).

As a comparison between cross-dating and dating based on assumed constant linear growth, a “constant-growth” date for peak Ba/Ca was determined by linearly dating shells between the collection date (8 July) and the last cross-dated growth increment (11 February). As determined by cross-dating, the large Ba/Ca peak occurred between 28 March and 3 April, whereas the constant-growth-based approach placed this peak between 5 April and 1 May. Thus, if constant growth was used to date growth increments, shell-environmental correlations would be off by more than a month, and peaks in Ba/Ca/shell would not be synchronous.

While no quantitative sub-annual study comparing growth-increment back-counting to cross-dating could be found, Black et al. (2008) compared cross-date-determined ages to back-count-determined ages for 432 geoduck bivalves (Panopea abrupta) from British Columbia, Canada finding that ages agreed for only 21% of the samples. For the remaining specimens, cross-date-determined ages were younger than the back-count determined age in 72% of the shells and 21% of the shells had older cross-dated-determined ages than the back-counting-determined ages.

Even in shells with clear sub-annual banding, the ability to reliably date growth increments by back-counting is limited due to growth irregularities from to disturbance and shutdown, e.g., Schöne et al. (2002). Additionally, back-counting does not provide a statistical

Table 1
Pearson product moment correlation coefficients for cross-dated Ba/Ca and environmental variables, significant (p < 0.01) correlations are in bold and number of sets used in parentheses. Offset refers to the number of days Donax Ba/Ca date were moved back in time.

<table>
<thead>
<tr>
<th>Offset</th>
<th>0 day</th>
<th>−3 day</th>
<th>−6 day</th>
<th>−9 day</th>
</tr>
</thead>
<tbody>
<tr>
<td>Chlorophyll a</td>
<td>0.07 (62)</td>
<td>0.23 (67)</td>
<td>0.41 (60)</td>
<td>0.54 (62)</td>
</tr>
<tr>
<td>Nitrate</td>
<td>0.30 (62)</td>
<td>0.68 (67)</td>
<td>0.27 (50)</td>
<td>0.06 (62)</td>
</tr>
<tr>
<td>Phosphate</td>
<td>0.00 (62)</td>
<td>0.50 (67)</td>
<td>−0.13 (60)</td>
<td>−0.11 (62)</td>
</tr>
<tr>
<td>Silicate</td>
<td>−0.18 (62)</td>
<td>0.42 (67)</td>
<td>0.15 (60)</td>
<td>0.17 (62)</td>
</tr>
<tr>
<td>Nitrite</td>
<td>0.04 (62)</td>
<td>0.46 (67)</td>
<td>0.03 (60)</td>
<td>−0.09 (62)</td>
</tr>
<tr>
<td>Ammonium</td>
<td>0.13 (62)</td>
<td>0.10 (67)</td>
<td>−0.17 (60)</td>
<td>−0.10 (62)</td>
</tr>
<tr>
<td>Total diatoms</td>
<td>0.28 (27)</td>
<td>−0.17 (30)</td>
<td>0.21 (30)</td>
<td>−0.23 (21)</td>
</tr>
<tr>
<td>Pseudo-nitzschia spp.</td>
<td>0.05 (27)</td>
<td>−0.31 (30)</td>
<td>0.38 (30)</td>
<td>−0.30 (21)</td>
</tr>
<tr>
<td>Total dinoflagellates</td>
<td>−0.24 (27)</td>
<td>0.14 (30)</td>
<td>0.39 (30)</td>
<td>0.32 (21)</td>
</tr>
<tr>
<td>L. polyedrum</td>
<td>−0.26 (27)</td>
<td>0.15 (30)</td>
<td>0.44 (30)</td>
<td>0.35 (21)</td>
</tr>
<tr>
<td>SST</td>
<td>−0.12 (73)</td>
<td>−0.09 (75)</td>
<td>0.00 (75)</td>
<td>−0.10 (75)</td>
</tr>
<tr>
<td>Salinity</td>
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<td>0.04 (75)</td>
<td>0.05 (75)</td>
<td>−0.05 (75)</td>
</tr>
<tr>
<td>Density (bottom)</td>
<td>0.15 (73)</td>
<td>0.09 (74)</td>
<td>0.14 (73)</td>
<td>0.19 (75)</td>
</tr>
</tbody>
</table>

Fig. 5. (A) Ba/Ca determination of four D. gouldii shells collected on 8 July 2008. (B) Total diatom and dinoflagellate counts, total dinoflagellates peaked twice, once in March and once in May. While total diatoms had three peaks the largest in early June. Dinoflagellates were primarily responsible for the Chl a peak seen in late March. Note diatoms and dinoflagellates are on separate axis. (C) Counts of L. polyedrum dinoflagellates and Pseudo-nitzschia spp. diatoms with Chl a plotted against the right y-axis. (D) Concentrations of nitrate and silicate on the left y-axis and phosphate and ammonium on the right y-axis.
framework to relate growth increments between shells from the same collection nor does it allow for shells with different collection times to be correlated. In contrast, cross-dating allows shell chronologies to span areas of growth shutdown and irregularities with an exact date assigned to growth increments. Cross-dating growth increments provides a dating based on an exogenous environmental rhythm compared with matching instrumental seawater temperature to shell based temperature which can be prone to time-averaging and seawater δ¹⁸O variations (Goodwin et al., 2004).

4.2. Relationship among chlorophyll a and phytoplankton

Phytoplankton community data are necessary to interpret Chl a measurements with respect to species composition and abundance. In coastal San Diego, phytoplankton blooms are commonly dominated by diatoms and/or dinoflagellates (Allen, 1920). Over a majority of the study period, diatoms were roughly seven times more abundant than dinoflagellates, however, peaks in Chl a resulted from increased dinoflagellates, including the increase in Chl a during 17 March–7 April which was driven by an increase in the dinoflagellate L. polyedrum. The phytoplankton community data show two peaks in dinoflagellate abundance roughly equal in size. The first peak occurred in mid-March, coinciding with a large Chl a peak, was dominated by L. polyedrum. The second peak occurred in late April to early May, dominated by Akashiwo sanguinea, Prorocentrum spp., and Ceratium spp., and did not coincide with a large Chl a peak. Diatom cell abundance through the study interval showed three peaks, with the first two peaks (24 March and 5 May) dominated by Chaetoceros spp. and Leptocylindrus spp. and the third much larger peak (2 June) dominated by Pseudo-nitzschiia spp. within the delicatissima group. None of these three diatom cell abundance peaks coincided with a marked increase in Chl a. However, the first diatom peak coincided with the largest influx of nitrate (8.83 μmol/L) and silicate (10.65 μmol/L) during the study interval, indicating that this water parcel recently arrived to the euphotic zone, and the second diatom peak occurred with the second highest influx of nitrate (3.22 μmol/L). Thus, weekly-resolution phytoplankton assemblages are influenced by nutrient input, but are poorly related to the available bi-weekly-resolution Chl a concentration. Prior studies at this location have also found increased diatom abundance associated with the influx of nitrate near the coast (Kamykowski, 1974; Goodman et al., 1984) and negative sea surface temperature anomalies prior to nutrient peaks (Allen, 1920).

Chl a concentration and phytoplankton cell abundance are two parameters used to estimate phytoplankton biomass. Chl a is used to estimate phytoplankton biomass based on assumptions to the amount of Chl a per cell and size of cells, whereas cell counts directly enumerate the abundance of cells per liter. Chl a based biomass estimates can vary independently of actual biomass due to size of cell, health, life stage, and taxonomy of the cells, as well as current growing conditions including light and nutrients. Therefore different growing conditions and stages as well as changes in plankton communities can alter these estimates of biomass. Based on size-fractionated chlorophyll measurements from the SIO Pier (unpublished M. Carter), on average 67% of the chlorophyll biomass consists of phytoplankton greater than 3 μm. Due to variability in phytoplankton species composition, the hypothesis that increased chlorophyll concentration is driven by increased diatom abundance is not valid in this area. Increases in chlorophyll concentration may also be due to increased abundance of dinoflagellates or picoplankton which may not be related to upwelling events.

In the study region, local productivity and nutrient delivery is controlled by local events (e.g., internal waves, tidal bores, and longshore transport) rather than regional wind-driven upwelling. Thus, any attempt to use regional datasets (e.g., CalCOFI, satellite-derived SST, Chl a) would lead to an erroneous correlation of these data to local shell-derived patterns. Without local records, calibrating shell based signals to environmental variability can lead to false correlations.

4.3. Relation of Ba/Cashell to phytoplankton

Ba/Cashell was significantly correlated to the Chl a from six and nine days prior; a finding consistent with other studies of bivalves To test the degree to which these correlations were driven by peak values, the two highest Chl a measurements (11.6 and 9.3 μg/m³) were removed from the analysis and both correlations remained significant. Ba/Cashell–Chl a correlation is not dependent on one coinciding peak but appear to remain significant for the entire study period.

The dinoflagellate L. polyedrum was highly abundant just prior to peak Ba/Cashell (Fig. 5) however, no significant relationship between L. polyedrum abundance and Ba/Cashell was found. Total dinoflagellate abundance showed two large peaks, one about a week before peak Ba/Cashell and one six weeks after (Fig. 5B). Diatom cell abundance and Ba/Cashell were not significantly correlated; diatoms were found in high abundance on 28 April, 12 May, 2 June, and 9 June, but none of these dates were associated with markedly elevated Ba/Ca values (Fig. 5B).

4.4. Relation of Ba/Cashell to physical environment

Ba/Cashell was significantly positively correlated with nitrate, phosphate, silicate, and nitrite from three days prior. Nitrogen and phosphate are two important macronutrients necessary for phytoplankton growth. Nitrate, nitrite, and phosphate have a nutrient-type vertical profile with low concentration in surface water and increased concentration below the mixed layer. High concentrations of nitrate in surface waters, as seen in late March, suggests recently upwelled water. At depth, silicate and nitrate occur in a nearly 1:1 ratio, but in the mixed layer nitrate is quickly scavenged. Using this 1:1 relationship, silicate can be used as proxy for the nitrate content of water before it advected into the mixed layer and can be used to date the relative age of upwelled water (Dugdale and Wilkerson, 1998). For example, the peak in nitrate in late March is nearly equal in concentration to silicate, indicating that the water parcel was recently upwelled. If the water parcel was upwelled a relatively longer time ago, then it would be expected that silicate would remain high and nitrate would be low. Recently upwelled water would also contain relatively higher concentrations of other elements not quantified in this study (e.g. barium) compared to other surface waters. Ammonium was not significantly correlated with Ba/Cashell. The oxidation of ammonium to nitrite occurs in surface waters and is typically associated with recycled productivity.

In this study, D. gouldii were collected from a well-mixed sandy-beach environment far from any freshwater point-source and salinity was relatively constant throughout the study interval with no major deviations during intervals of elevated Ba/Cashell. The nearest rainfall measured at the SIO pier occurred two weeks (16 March) before the elevated Ba/Cashell with 0.31 cm of precipitation in a day. During peak Ba/Cashell, factors which would result in increased ground water discharge (seismic activity or upland precipitation) remained constant. Thus, a freshwater-related mechanism (via an assumed inverse relationship between salinity and seawater Ba/Ca ratios; e.g., Gillikin et al. (2006)) cannot be invoked to explain the observed peaks. Temperature has been reported to be positively related to Ba/Cashell in larval oysters (Carson, 2010) and negatively related to Ba/Cashell in larval gastropods (Zacherl et al., 2003). In this study, temperature is weakly negatively correlated with Ba/Cashell and no temperature deviation coincided with the observed major Ba/Ca peak.

In coastal San Diego, seawater density can be used as a proxy for nitrate, although the dynamics tend to be non-linear.
2010). Typically the nutrient line is at densities around 25.1 σ, with <25.1 σ, water being nitrate-poor and >25.1 σ, being nitrate-rich. The late March peak in nitrate and silicate occurs at the same time seawater density is >25.1 σ, suggesting that this nutrient peak was due to upwelling rather than runoff- or groundwater-related nutrient input (Fig. 3C).

The question remains whether the peaks in Ba/Ca in biogenic carbonates have been attributed to a plethora of environmental and biological factors including proximity to riverine and groundwater supply (Shaw et al., 1998; Carroll et al., 2009), seawater temperature (Zacherl et al., 2003, 2009; Carson, 2010), gonad development and spawning (Gillikin et al., 2006), seawater Ba/Ca concentrations (Lea et al., 1989), and diatom abundance (Thébault et al., 2009). The inverse relationship between salinity and Ba/Ca seawater is reflected in Ba/Cashell, for example, Gillikin et al. (2006) found a negative relationship between salinity and background Ba/Cashell in estuarine-reared Mytilus edulis shells. Based on environmental data, we find no support for either a salinity- or temperature-based mechanism for the observed Ba/Cashell peak. Elevated bivalve Ba/Ca has also been hypothesized to result from internal remobilization of Ba from tissues to skeletal carbonate during spawning (Gillikin et al., 2006). In D. gouldii, specimens with shell lengths of less than 9 mm typically do not have differentiated gametes and specimens over 9 mm could be part of the spawning population (Winter and Hatch, 2010). To assess the shell lengths for the four specimens when the major Ba/Ca peak was observed, a D. gouldii shell height:length relationship was calculated (height = 0.65 × length − 0.045, r² = 0.98) based on 47 specimens ranging in length from 5.25 to 20.8 mm. Using this relationship and the analyzed thin sections of the analyzed shells A–D during their observed Ba/Ca peaks were estimated at 13.3, 12.4, 11.8, and 13.6 mm, respectively. Based on these data, the D. gouldii specimens would have had differentiated gonads and could have spawned. However, D. gouldii are serial broadcast spawners (Haderlie and Abbott, 1980) and likely would have spawned multiple times during the represented four months of life. If so, the spawning event was responsible for elevated Ba/Ca values, multiple elevated Ba/Ca values or at least a step-wise increase in “background” Ba/Ca values would be expected, and no such pattern was observed. Therefore, similar to Gillikin et al. (2008), we reject a spawning-related mechanism for the observed Ba/Cashell peak.

The remaining hypotheses to explain Ba/Ca peaks in biogenic carbonates are (1) increased consumption of barium-rich particles such as diatoms, and (2) ambient increases in seawater Ba/Ca. The diatom-ingestion hypothesis invokes a mechanism where filter-feeding bivalves digest barite or barite-rich particles then digest Ba is transported via extrapallial fluid to calcification sites and is incorporated in the shell carbonate (Stecher et al., 1996). Prior studies using Chl α as a proxy for diatom abundance, found that Chl α peaks and coinciding Ba/Cashell peaks frequently co-occur (Vander Putten et al., 2000; Thébault et al., 2009). In Mytilus edulis, broad and marked Ba/Cashell peaks (~30 μmol/mol) have been observed lasting ~20 days and coincide with intervals of high Chl α (Vander Putten et al., 2000). However, the relationship between Chl α and Ba/Cashell is not linear and Chl α peaks occur without corresponding Ba/Cashell peaks (Vander Putten et al., 2000). Thébault et al. (2009) present compelling data where a large Chl α peak occurs a week before a large Ba/Cashell peak in the tropical scallop Pseudotaxodina radula; the authors assume that this Chl α peak is due to a diatom bloom and that the Ba/Cashell peak resulted from ingestion of these Ba-rich diatom frustules. However, the data also contain a smaller Ba/Cashell peak that preceded the aforementioned Chl α peak by ~14 days as well as a Chl α peak not associated with a Ba/Cashell peak. The authors attribute the occurrence of a Ba/Cashell peak before a Chl α peak to dating errors resulting from back-counting growth increments, even though this peak occurs near the commissure, where back-counting would be most accurate. In a similar study, Barats et al. (2009) compared the Ba/Cashell of the North Atlantic scallop P. maximus to a suite of environmental parameters, but unlike the previously mentioned studies, they measured seawater particulate and dissolved barium concentrations as well as abundances of the diatoms Chaetoceros spp. and the dinoflagellate Gymnodioum spp. The researchers found that seawater Ba to Ba/Cashell partition coefficients were comparable to previously published values (e.g., DBa ~0.2), based on average seawater dissolved barium and background (non-peak) Ba/Cashell. (Gillikin et al., 2006; Gillikin et al., 2008). Episodically elevated Ba/Cashell peaks coincided with elevated dissolved Ba concentrations, but were much higher than predicted by partition coefficients. These researchers concluded that Ba/Cashell peaks cannot be attributed to diatom abundance or any relevant paleoproductivity tracer (e.g., Chl α).

While markedly coincident peaks in Chl α and shell Ba/Ca are visually compelling, the broader often variable and non-linear relationship between Chl α and Ba/Cashell as well as the existence of peaks in one variable without commensurate peaks in the other variable currently limit the utility of Ba/Cashell as proxy for primary productivity (Gillikin et al., 2008). This study compared high resolution Ba/Cashell and environmental data in a robust temporal framework, and found significant correlations between Ba/Cashell and Chl α from and six and nine days prior, with Chl α from nine days prior showing a higher correlation. While other studies have found a similar correlation between Chl α and Ba/Cashell, these studies attribute their Chl α increase to diatoms whereas this study demonstrates that the Chl α is not a universal proxy for diatoms and, in fact, Chl α is not specific to any taxon or group. Furthermore, the covariance of upwelled nutrients, which presumably included Ba, and the phytoplankton communities which flourish due to increased nutrients, needs to be addressed before any Ba/Cashell–Chl α proxies are utilized. In this system, the Chl α peak which occurs six to nine days prior to peak Ba/Cashell appears primarily due to the relatively large dinoflagellate L. polyedrum rather than diatoms (Fig. 5B).

In bivalves, non-peak Ba/Cashell values are often low (0.2–2.0 μmol/mol; see Table 2 in Barats et al. (2009)), and these values are dependent on seawater Ba with seawater - shell partition coefficients (DBa) of 0.07–0.18 (Gillikin et al., 2006; Gillikin et al., 2008), however, Ba/Cashell peaks are frequently attributed to environmental or biological factors. In corals and foraminifera, peak and non-peak Ba/Cashell values are used as a proxy for seawater Ba/Ca values based on a DBa of 1.3 and 0.17–0.22, respectively (Lea et al., 1989; Lea and Boyle, 1991). Although seawater Ba concentrations for this study area and interval are not known, Carson (2010) found seawater Ba near the mouth of San Diego Bay to vary from 13.7 to 66.0 nmol/kg from spring to fall during 2006 and 2007. Seawater Ba was also sampled in 1998 as a continuous surface transect from southern Baja Mexico to San Diego and typical averaged 30–35 nmol/kg with deviations down to 13 nmol/kg occurring over small spatial scales (~100 km) (Esser and Volpe, 2002). To place the observed Ba/Cashell in the context of these regional seawater Ba/Ca values, a DBa can be estimated using the average non-peak for Ba/Cashell (i.e., 3.47 μmol/mol) and “normal” surface Ba concentrations for the area (36 nmol/kg; Esser and Volpe, 2002), which produces a DBa of 0.95. While this estimated DBa is higher than previously observed for other aragonitic bivalves, the background shell Ba/Ca ratios are also higher than many other studied species as well. However, abiotic aragonite has a DBa of >0.5 (Dietzel et al., 2004; Gaetani and Cohen, 2006) and corals often have a DBa of ≥1.0 (Lea et al., 1989; Alibert et al., 2003). Using a DBa of 0.95, the seawater Ba concentration necessary to fully explain observed values in D. gouldii would range from...
20.9 to 118.0 nmol/kg. Both regional studies reported values lower than 20.9, but the highest observed seawater Ba concentration was 66.9 nmol/kg (Carson, 2010). Although the barium concentrations measured by Carson (2010) are just over half what would be required to directly explain shell Ba/Ca, these data have a resolution of 2–3 weeks, which might not detect high frequency changes in Ba concentration. Using seawater Ba on data from Carson (2010) and Esser and Volpe (2002), much of the “background” variation observed in Ba/Ca\textsubscript{shell} can be explained by variations in seawater Ba concentrations. The highest Ba/Ca\textsubscript{shell} measurement of 11.29 μmol/mol would require a seawater Ba concentration of 118.0 nmol/kg, while such a seawater value has been observed in the deep ocean, it is difficult to evaluate the likelihood of such a value in the surf zone (Chan et al., 1977). In support of the seawater Ba hypothesis, nutrients were high on 27 March just prior to the observed peak in Ba/Ca\textsubscript{shell} (Fig. 5D), and the nitrate and silicate values were roughly equal, consistent with recent delivery of nutrient rich water to the euphotic zone. Barium, like nitrate, has a nutrient-type profile and is quickly removed from surface waters by primary producers. Therefore, the same upwelling event which resulted in high nitrate values would have, most likely, resulted in high dissolved barium concentrations. This conjecture is difficult to assess without direct measurements of seawater barium, but certainly warrants further investigation.

5. Conclusion

Cross-dating has been successfully applied to day long and fortnightly growth increments, which allowed laser-ablated Ba/Ca\textsubscript{shell} determinations to be precisely dated with less error than either back-counting or assuming constant growth. The dated Ba/Ca\textsubscript{shell} ablations were then correlated with a robust set of environmental time-series, including temperature, salinity, density, phytoplankton, and dissolved nutrient concentrations. The cross-dated Ba/Ca\textsubscript{shell} determinations were significantly correlated with nitrate, nitrite, and phosphate concentrations days prior to Ba/Ca\textsubscript{shell} determinations with Chl \textalpha{} six and nine days prior. While a single driver for population wide synchronous peaks in Ba/Ca\textsubscript{shell} for bivalves remains enigmatic, this research highlights the methods necessary to create a well-constrained Ba/Ca\textsubscript{shell} chronology based on high frequency growth increments. Furthermore, these data show that diatom concentration occurs independent of Chl \textalpha{}, reinforcing the need for phytoplankton counts to assess the influence of phytoplankton on Ba/Ca\textsubscript{shell}.

This study supports the hypothesis that Ba/Ca\textsubscript{shell} peaks are due to environmental forcing, however the exact driver remains unclear. To better understand the nature of such Ba/Ca\textsubscript{shell} peaks, phytoplankton communities should be well described and seawater Ba/ Ca should be monitored. If diet-related hypotheses are to be tested, studies should include measurements of Ba/Ca values in the organisms (e.g., gut, hemolymph).

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