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

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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_{shell} is significantly correlated with Chl *a* from six and 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_{shell}. Transiently higher seawater Ba/Ca resulting from upwelling may be reflected in peak Ba/Ca_{shell}, however the exact mechanisms leading to population wide Ba/Ca peaks remains enigmatic.

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 Arrhenius, 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 (Monnin 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; Alibert and Kinsley, 2008).

In bivalves, Ba/Ca_{shell} ratios along shell growth profiles are typically relatively low (i.e., $<10\ \mu mol/mol$), 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/Ca_{shell} is broadly consistent with ambient seawater Ba concentrations with a Ba seawater–shell partition coefficients of 0.07–0.18 for both calcite

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and aragonite (Gillikin et al., 2006, 2008). In the aragonitic *Saxidomus giganteus*, ten years of continuous $\text{Ba/Ca}_{\text{shell}}$ show remarkably synchronous inter-individual variability, suggesting that $\text{Ba/Ca}_{\text{shell}}$ 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 $\text{Ba/Ca}_{\text{shell}}$ 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 $\text{Ba/Ca}_{\text{shell}}$ in the tropical New Caledonian scallop *Comptopallium 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 $\text{Ba/Ca}_{\text{shell}}$ in the temperate North Atlantic scallop *Pecten maximus*.

If $\text{Ba/Ca}_{\text{shell}}$ 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 $\text{Ba/Ca}_{\text{shell}}$ 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

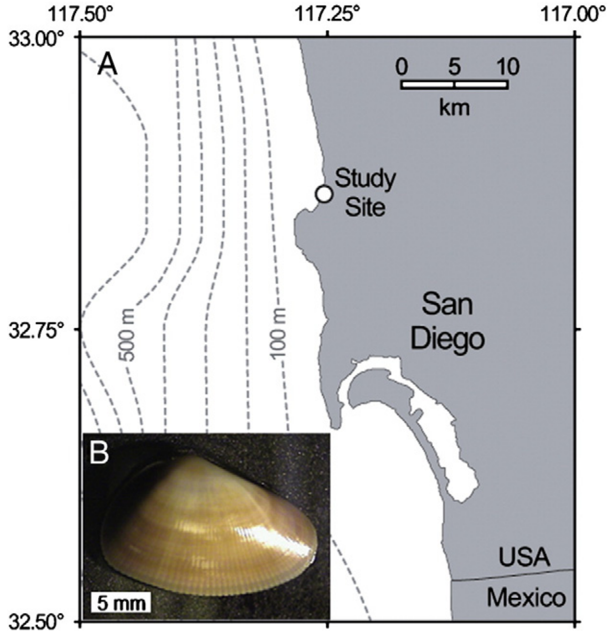

Fig. 1. (A) Map of San Diego County with Scripps Institution of Oceanography pier and beach marked as "Study Site". All environmental data come from the Scripps Institution of Oceanography pier and all *D. gouldii* were collected within 100 m of the pier. (B) Image of adult *D. gouldii* valve.

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 (σ_T).

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