Variations in seawater Sr/Ca recorded in deep-sea bamboo corals

T. M. Hill,[1,2] M. LaVigne,[1,2] H. J. Spero,[1] T. Guilderson,[3,4] B. Gaylord,[2] and D. Clague[5]

Received 1 December 2011; revised 18 May 2012; accepted 22 May 2012; published 4 July 2012.

[1] A depth transect of deep-sea bamboo corals along the California margin provides evidence that coral strontium to calcium ratios (Sr/Ca_{coral}) record seawater Sr/Ca ratios (Sr/Ca_{sw}). A calibration was constructed utilizing Sr/Ca_{coral} ratios and previously published Pacific Sr/Ca_{sw} data ($R^2 = 0.53$, $n = 12$, $p < 0.01$): Sr/Ca_{coral} (mmol/mol) = 4.62*Sr/Ca_{sw} (mmol/mol) − 36.64. Sr/Ca_{sw} is ultimately governed by the remineralization of Sr-containing shells of surface water-derived marine organisms (e.g., Acantharia) at intermediate water depths. California margin Sr/Ca_{coral} records from 792 and 1295 m document fluctuations in Sr/Ca_{sw} that appear decadal-scale. These results suggest that Sr/Ca_{sw} may not be as stable as previously assumed and may be influenced by surface productivity on short timescales.

Citation: Hill, T. M., M. LaVigne, H. J. Spero, T. Guilderson, B. Gaylord, and D. Clague (2012), Variations in seawater Sr/Ca recorded in deep-sea bamboo corals, *Paleoceanography*, *27*, PA3202, doi:10.1029/2011PA002260.

1. Introduction

[2] Deep sea bamboo corals, gorgonian octocorals named for their morphology of alternating calcite internodes and proteinaceous gorgonin nodes, are being used to reconstruct past ocean climate and chemistry [*Hill et al.*, 2011; *LaVigne et al.*, 2011; *Noé et al.*, 2008; *Roark et al.*, 2005; *Sinclair et al.*, 2011; *Thresher et al.*, 2004], including the use of trace elements such as Sr/Ca ratios [*Roark et al.*, 2005]. While there is some indication that seawater Sr/Ca ratios (Sr/Ca_{sw}) may have changed in the geologic past (5–10% over glacial/interglacial timescales [*Martin et al.*, 1999; *Stoll et al.*, 1999]), Sr/Ca_{sw} is typically assumed to exhibit limited variability in the modern ocean. However, a confounding factor on short-term modern Sr/Ca_{sw} variability at depth is the changing flux of plankton from the surface ocean [*De Deckker*, 2004; *de Villiers*, 1999; *Michaels*, 1988, 1991; *Stoecker et al.*, 1996]. An especially important source of such fluxes is Acantharia, a taxonomic group of surface-dwelling (50–200 m) protists that produce celestite ($SrSO_4$) shells. Although these organisms do not leave a fossil record in marine sediment, they impact deep sea Sr/Ca_{sw} due to complete shell dissolution at depth, inducing a peak in Sr/Ca_{sw} between 250 and 1500 m [*Brass and Turekian*, 1974; *De Deckker*, 2004; *de Villiers*, 1999; *MacKenzie*, 1964; *Michaels*, 1988, 1991; *Stoecker et al.*, 1996].

[3] In this investigation, we examine Sr/Ca ratios in bamboo corals sampled from the California margin (Table 1), near and within North Pacific Intermediate Water (NPIW; ∼400–1000 m) [*Reid*, 1965; *Talley*, 1988, 1993] and Pacific Deep Water (PDW; >1500 m) [*Bostock et al.*, 2010; *Johnson and Toole*, 1993]. Sr/Ca has been used as a proxy for growth rate and temperature in calcite-secreting organisms [e.g., *Sosdian et al.*, 2006; *Stoll et al.*, 2002, 2007]. However, it has been previously documented that Sr/Ca in bamboo corals is not closely linked to temperature [*Thresher et al.*, 2010]. While some studies have indicated that Sr/Ca in bamboo corals (Sr/Ca_{coral}) may be associated with short-term changes in growth rates dictated by surface-derived food sources, these patterns are not present in all bamboo corals [*Roark et al.*, 2005; *Sinclair et al.*, 2011; *Thresher et al.*, 2009; *Tracey et al.*, 2007]. Here we examine another potential mechanism, that Sr/Ca_{coral} is influenced by Sr/Ca_{sw} and therefore can be utilized to reconstruct past variability in Sr/Ca_{sw}.

2. Materials and Methods

[4] Bamboo corals (genera *Isidella*, *Keratoisis*, and *Lepidisis*) were collected via remotely operated vehicle or dredge from 250 to 2136 m water depth (Table 1). In most cases, corals possessed living polyps at the time of sampling so were assumed to be actively calcifiying. We utilized established sampling methods for bamboo corals [*Hill et al.*, 2011; *LaVigne et al.*, 2011; *Roark et al.*, 2005; *Thresher et al.*, 2010]. Sr/Ca_{coral} from outer margin calcite (most recent calcification) was determined for twelve corals using ICP-OES analyses, and compared to published Sr/Ca_{sw} data. For these analyses, two replicate powdered samples (∼1 mg) were extracted from the outer 1–2 mm of each of coral. Powdered samples were dissolved in 1N HNO_3 and analyzed for Sr/Ca at UC Davis Bodega Marine Laboratory via

[1]Department of Geology, University of California, Davis, California, USA.
[2]Bodega Marine Laboratory, University of California, Bodega Bay, California, USA.
[3]Center for Accelerator Mass Spectrometry, Lawrence Livermore National Laboratory, Livermore, California, USA.
[4]Institute of Marine Sciences, University of California, Santa Cruz, California, USA.
[5]Monterey Bay Aquarium Research Institute, Moss Landing, California, USA.

Corresponding author: T. M. Hill, Department of Geology, University of California, Davis, CA 95616, USA. (tmhill@ucdavis.edu)

0883-8305/12/2011PA002260

Table 1. Coral Samples Utilized in This Study[a]

Sample ID	Longitude (W)	Latitude (N)	Depth (m)	Identification
Bodega (BB)	−123.50	38.50	250	unknown
T661 A9	**−121.08**	**34.05**	**792**	***Isidella spp.***
T1101A17	−123.40	37.37	1005	*Isidella spp.*
T1101A13	−123.41	37.37	1011.9	*Isidella spp.*
T1100A21	−123.39	37.37	1077.9	*Isidella spp.*
T664 A17	**−120.91**	**33.13**	**1295**	***Keratoisis spp.***
T1102A13	−123.72	35.73	1453.1	*Isidella spp.*
T1102A05	−122.72	35.74	1615.3	*Keratoisis spp.*
T664A2	−120.89	33.15	1954	*Lepidisis spp.*
T669 A1	**−121.48**	**32.64**	**2043**	***Isidella spp.***
T664A1	−120.88	33.15	2055	*Isidella spp.*
T668 A13	**−120.05**	**31.91**	**2136**	***Keratoisis spp.***

[a]All corals are from the California margin. Corals were collected via submersible in 2004 or 2007, with the exception of BB, collected via dredge. All coral specimens were utilized to sample outer edge calcite to compare to ambient seawater Sr/Ca composition via ICP-OES analyses. Four corals in bold are the focus of LA-ICP-MS analyses. Where possible, species identifications were made during shipboard sampling.

solution ICP-OES (JY Ultima 2 C). The analytical reproducibility for solution Sr/Ca measurements on an in-house matrix-matched bamboo coral consistency standard was ±1.3% RSD (n = 8).

[5] Four of the twelve corals (Table 1) were also thin sectioned (>100 um thickness) and polished for laser ablation-inductively coupled plasma mass spectrometry (LA-ICP- MS) analyses. Sr/Ca ratios via LA-ICP-MS were determined at UC Davis using a New Wave Research UP-213 laser ablation system equipped with a Nd: YAG deep UV-213 nm laser with Supercell, and an Agilent Technologies 7500a ICP-MS. The LA-ICP-MS analyses utilize a 15 Hz repetition rate, He sweep/carrier gas, and an individual circular 40 μm spot size (100 μm spacing). LA-ICP-MS data were acquired from outer margin to the center of the coral, following the growth axis (most recent to oldest material). Raw count rates were calibrated using a NIST-612 glass standard with periodic measurement of NIST 612 and USGS standard MACS-1 during the five day analytical period to determine accuracy, precision and instrumental drift. Off-line data analysis and blank correction were performed using *Glitter* data reduction software. Repeat analyses of MACS-1 indicated concentrations (206–242 ppm) consistent with the established range of Sr concentrations for this standard (200–240 ppm; USGS [*Strnad et al.*, 2009]). Reproducibility of the Sr/Ca data was assessed by two mechanisms. First, repeated analyses of MACS-1 over multiple days (24 analyses, 2 days) yielded a SD of +/−0.04 mmol/mol. Additionally, parallel LA-ICP-MS tracks were collected from outer margin toward the center of coral sample T669 A1, yielding a reproducibility of +/−0.03 mmol/mol, based on the reproducibility of the mean of 30 points analyzed twice over 2 days. These data correspond to a ±0.85–1.05% precision on the LA-ICP-MS Sr/Ca_{coral} measurements.

[6] Using a comparison of four corals in this study, the range of Sr/Ca_{coral} ratios obtained via LA-ICP-MS for the outer 1 mm of the coral skeletons are found to be within +/−0.21 mmol/mol of solution ICP-OES analyses of the same coral (Table 2). We attribute the offsets between the two analytical methods to be a result of non-matrix match standardization by LA-ICP-MS (use of NIST glass

Table 2. Comparison of Coral Samples Analyzed Via ICP-OES and LA-ICP-MS[a]

Sample ID	ICP OES (mMol/mol)	LA-ICP MS (mMol/mol)
T661 A9	3.246 +/− 0.025	3.460 +/− 0.035
T669 A1	3.156 +/− 0.012	3.029 +/− 0.025
T668 A13	3.052 +/− 0.042	3.086 +/− 0.028
T664 A17	3.163 +/− 0.013	3.068 +/− 0.031

[a]Samples for ICP-OES were drilled from the outer 1–2 mm and analyses reflect the mean of 2 discrete samples. Samples for LA-ICP-MS were ablated from outer 1 mm and reflect a mean of 10 discrete samples; 1σ error ranges shown.

standards) and small day to day variability in LA-ICP-MS. Therefore, we plot LA-ICP-MS data as anomalies from mean Sr/Ca_{coral}; this method simultaneously removes variability associated with potential species-specific offsets given that results from three different species are reported here.

[7] Two of the four corals sampled at depths of peak Acantharia remineralization were further investigated in time series (T661 A9, 792 m and T664 A17, 1295 m). These specimens were tied to independent chronologies based upon multiple calcite radiocarbon dates in each coral (Table 3), and a modern tiepoint dictated by the fact that both corals were sampled alive in 2004 (i.e., youngest age = 2004). These chronologies rely on the long-term average extension rate, which is preferred over relying on intermittent growth band counts [*Hill et al.*, 2011; *LaVigne et al.*, 2011; *Noé et al.*, 2008]. The corals were sampled for radiocarbon analyses using a drill press (500 μm diameter bit). Radiocarbon analyses follow standard methods outlined in *Hill et al.* [2011]. Results are reported as conventional (uncorrected) radiocarbon age and per mil (‰) $D^{14}C$ as per international convention put forth in *Stuiver and Polach* [1977] where:

$$D^{14}C = \left[\left(\left({}^{14}C/{}^{12}C_{sample}\right)/\left({}^{14}C/{}^{12}C_{1950}\right)\right) - 1\right] \times 1000.$$

Table 3. Radiocarbon Measurements and Calculated Growth Rates[a]

Distance From Edge (mm)	^{14}C age	+/−	$D^{14}C$ (‰)	+/−	Calculated Growth Rate (mm/yr)
			Sample T661 A9		
0–1	1635	30	−189.7	2.7	0.048 +/− 0.015
5–6	1740	35	−194.6	3.1	0.063 +/− 0.044
7.5–8.5	1780	60	−204.3	5.1	
Average growth rate					0.055
			Sample T664 A17		
0.5–1.5	2010	35	−221.3	3.0	0.144 +/− 0.094
5.0–6.5	2050	40	−225.3	3.6	0.160 +/− 0.118
9.5–10.0	2075	30	−227.7	2.7	
Average growth rate					0.152

[a]One average extension rate is applied to each coral, because variability of extension rates from one sample to another fall within the margin of error. Previous research comparing growth band features with radiocarbon-based growth rates indicate that these two methods are typically consistent with one another but growth bands are not always identifiable in bamboo corals and can exhibit extremely variable extension rates instead of capturing a long-term average [*Hill et al.*, 2011; *LaVigne et al.*, 2011].

The radiocarbon "age" of the calcite skeleton reflects that of the surrounding DIC, based upon previous results comparing bamboo corals and ambient seawater DIC from the California margin [*Hill et al.*, 2011; *Roark et al.*, 2005]. Corals T661 A9 and T664 A17 exhibit radiocarbon ages of 1635 +/−30 and 2010 +/−35 years, respectively, consistent with corals and seawater from intermediate depths along the California margin [*Hill et al.*, 2011]. To construct a chronology, extension rates calculated from three radiocarbon ages for each coral are averaged to generate *one* extension rate for each coral (variability of extension rates from one sample to another fall within the margin of error; Table 3). We consider this method to be a 'conservative' approach to understanding coral growth and chronology, because it does not attempt to account for changes in growth that may have occurred throughout the lifetime of the coral.

3. Coral Sr/Ca Proxy

[8] Although existing Sr/Ca_{sw} data are sparse, we compare solution phase Sr/Ca_{coral} data from twelve specimens (outer 1–2 mm margin samples; 250–2136 m water depth) with published water column Sr/Ca_{sw} ratios collected from two transects in the western Pacific (10°S, 179°E; 45°N, 179°E; Figure 1) [*de Villiers*, 1999]. Powdered samples extracted from the outer 2 mm of coral calcite reflect an average of one decade of coral growth, based upon the range of bamboo coral growth rates reported here and in *Hill et al.* [2011]. Very few water column Sr/Ca_{sw} data are available for comparison, so these sites, although geographically distant, provide the best opportunity for Sr/Ca calibration. The transect from 10°S exhibits a depth zone characterized by increased Sr/Ca_{sw} from ∼250–1600 m, consistent with previous observations by *Brass and Turekian* [1974] (Figure 1). The transect from 45°N exhibits a slightly deeper zone of increased Sr/Ca_{sw}, extending to 2000 m. An analogous peak in Sr concentration is also apparent at 700 m in a very low resolution water column profile from the Northeast Pacific (28°N, 121°W) [*Brass and Turekian*, 1974]. Sites investigated in the Atlantic present a similar vertical gradient [*de Villiers*, 1999]. [*de Villiers*, 1999] propose that the higher surface Sr/Ca_{sw} ratios at the 45°N site (relative to the 10°S site) reflect higher nutrient composition (thus, higher productivity) of these waters; this may also explain the broader depth zone of increased Sr/Ca_{sw} at the 45°N site. Sr/Ca_{sw} is also influenced by water mass history, with higher preformed ratios in the deep Pacific than in the North Atlantic [*de Villiers*, 1999].

[9] Sr/Ca_{coral} ratios from within the zone of elevated Sr/Ca_{sw} track the water column Sr/Ca_{sw} trends, exhibiting

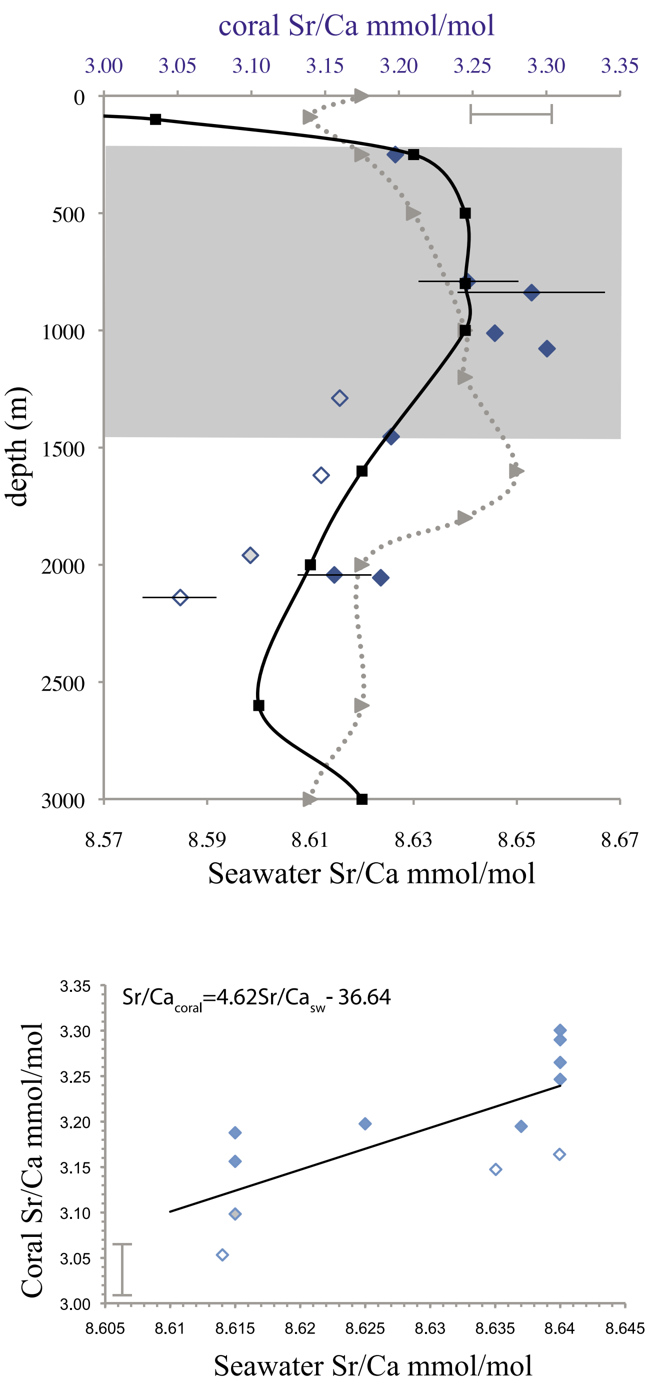

Figure 1. (top) Depth transects of water column Sr/Ca (mmol/mol; error < 0.05%) at 10°S, 179°E (black squares, solid line), and 45°N, 179°E (gray triangles, dashed line) [*de Villiers*, 1999] and California margin bamboo coral Sr/Ca (mmol/mol; diamonds, no line). Filled diamonds represent corals identified as *Isidella* spp. or unknown species. Unfilled diamonds represent corals identified as *Keratoisis* spp. Diamond with light gray fill: coral identified as *Lepidisis* spp. Each Sr/Ca_{coral} point reflects an average of two samples acquired from the edge of the coral (average 1σ error ± 0.026 mmol/mol; error bar top right). Bars on four corals reflect the range of Sr/Ca_{coral} values observed in time series data as shown in Figure 2. Shaded region denotes depths of increased Sr/Ca_{sw} due to remineralization of Acantharia based upon observations of *Brass and Turekian* [1974]. (bottom) Sr/Ca_{sw} data via a compilation of the water column transects above, compared to coral samples at discrete depths (within 100 m of water samples). Two corals from depths not sampled by *de Villiers* [1999], are compared to linearly interpolated points using the full water column data set. This analysis yields a statistically significant relationship ($p < 0.01$) between Sr/Ca_{coral} and Sr/Ca_{sw}. Sr/Ca_{coral} error bar at bottom left, symbols as above.

Table 4. Coral Geochemistry[a]

Sample ID	Depth (m)	ICP OES (mMol/mol)	Temperature (°C)	Salinity (psu)	D Value
Bodega (BB)	250	3.198	7.5	34.2	0.371
T661 A9	792	3.246	4.5	34.4	0.376
T1101 A17	839	3.290	4.0	34.4	0.381
T1101 A13	1011.9	3.265	3.5	34.4	0.378
T1100 A21	1077.9	3.300	3.5	34.5	0.382
T664 A17	1295	3.163	3.5	34.5	0.366
T1102 A13	1453.1	3.195	2.5	34.5	0.370
T1102 A05	1615.3	3.148	2.5	34.5	0.365
T664 A2	1954	3.099	2.0	34.5	0.360
T669 A1	2043	3.156	2.0	34.6	0.366
T664 A1	2055	3.188	2.0	34.6	0.370
T668 A13	2136	3.052	2.0	34.6	0.354

[a]ICP-OES solution based analyses, reflecting an average of two samples for each coral. Temperature and salinity from *Levitus* [1994]. Calculated D-values for each coral are shown and described in the text.

elevated Sr/Ca_{coral} ratios (3.20–3.30 mmol/mol) relative to those sampled from below this depth (3.05–3.18 mmol/mol; Figure 1, top). The observation that Sr/Ca_{coral} changes with depth has been previously made in another bamboo coral study, based in the Southern Ocean and Western Pacific [*Thresher et al.*, 2010]. It is also possible to develop a more direct comparison of Sr/Ca_{coral} to Sr/Ca_{sw}, by compiling a master water column profile of Sr/Ca_{sw} ratios from across depths spanning those where coral samples were acquired (within ±100 m). This task is accomplished by merging the two Pacific Sr/Ca_{sw} transects [*de Villiers*, 1999], averaging when possible their respective points at each discrete coral sample depth. In the case of the two corals that were acquired from depths not sampled by *de Villiers* [1999], an estimated value of Sr/Ca_{sw} was determined by linear interpolation of points from the master water column data set. This analysis yields a statistically significant relationship ($R^2 = 0.53$, $n = 12$, $p < 0.01$) between Sr/Ca_{coral} and Sr/Ca_{sw} (Figure 1, bottom):

$$Sr/Ca_{coral}(mmol/mol) = 4.62{*}Sr/Ca_{sw}(mmol/mol) - 36.64$$

This correlation suggests that Sr/Ca_{sw} exerts considerable control on $Sr/Ca_{coral.}$ Based upon these data, we calculate a partition coefficient of D = 0.35–0.38 (where $D = Sr/Ca_{coral}/Sr/Ca_{sw}$; Table 4). These values are comparable to those of other taxa. For example, D values for foraminifera, gastropods, coccolithophores are 0.15, 0.18, and 0.32 respectively, calculated utilizing published $Sr/Ca_{calcite}$ data and a surface ocean average Sr/Ca_{sw} of 8.55 [*de Villiers*, 1999; *Sosdian et al.*, 2006; *Stoll et al.*, 1999, 2002]. Similarly, D values for fish otoliths, primarily controlled by Sr/Ca_{sw}, range from 0.18 to 0.34 [*Bath et al.*, 2000; *Phillis et al.*, 2011]. The inclusion of multiple coral species does not bias the regression, as the slope of the line resulting from inclusion of only *Isidella* samples does not differ significantly from the full regression ($t = 0.60$, $p > 0.5$).

[10] Variability in the twelve Sr/Ca_{coral} samples is larger (2.35%) than the observed Sr/Ca_{sw} variability across the same depth range (0.4%). This may in part be due to the temporal and spatial differences between the coral and water sampling – water sampling occurred at a single, discrete time, whereas the outer 2 mm of coral calcite reflects approximately a decade of growth, thus incorporating seasonal and annual variability in Sr/Ca_{sw}. The total global Sr/Ca_{sw} variability documented by *de Villiers* [1999] was 2–3%, placing the Sr/Ca_{coral} variability within the range of observed Sr/Ca_{sw} variability.

[11] Sr/Ca_{sw} exhibits a predictable relationship with other seawater nutrients, such as phosphate [*Brass and Turekian*, 1974; *de Villiers*, 1999]; based upon this, we can predict that corals along the California margin would experience a wider range of Sr/Ca_{sw} values (with depth, and perhaps temporally) than those in the western Pacific (Figure S1 in the auxiliary material).[1] Another possible driver of an increased Sr/Ca_{coral} gradient with depth (relative to Sr/Ca_{sw} plotted here) may be biases associated with the timing of calcification (e.g., if corals calcify faster during time periods of increased food/nutrients); however, very little is known about the temporal patterns of bamboo coral calcification rates. While no statistical relationship exists between Sr/Ca_{coral} and parameters such as temperature and salinity (Table 4), there is an inverse relationship between depth (pressure) and Sr/Ca_{coral} (r^2 0.48, $p < 0.02$); however, Sr/Ca_{sw} and depth (pressure) covary so cannot be distinguished as separate mechanisms influencing Sr/Ca_{coral}. The relationship between Sr/Ca_{coral} and depth may represent the effect of food quantity/quality to the corals, which could influence growth rate. However, we note that in four corals studied here, where it was possible to measure growth band width, there is no reliable statistical relationship between band width and Sr/Ca_{coral} (Figure S2), a finding supported by another trace elemental investigation in bamboo corals [*Sinclair et al.*, 2011].

4. A Centennial Scale Record of Sr/Ca Variability

[12] We plot Sr/Ca_{coral} anomalies for four corals from margin to edge of the coral (e.g., most recent to oldest coral growth; Figure 2). Sr/Ca_{coral} ratios from two Pacific corals located within PDW and below the celestite remineralization zone (2043 m and 2136 m) remain relatively stable (SD ± 1.15 and 0.98% of the mean, respectively; Table 5 and Figure 2), as one would expect for a depth region absent of strong Sr inputs. In contrast, the two corals from shallower sites near the deeper boundary of NPIW (792 m and 1295 m) exhibit higher Sr/Ca variability (SD ± 1.47 and 2.00% of mean, respectively; Table 5 and Figure 2). This dichotomy

[1]Auxiliary materials are available in the HTML. doi:10.1029/2011PA002260.

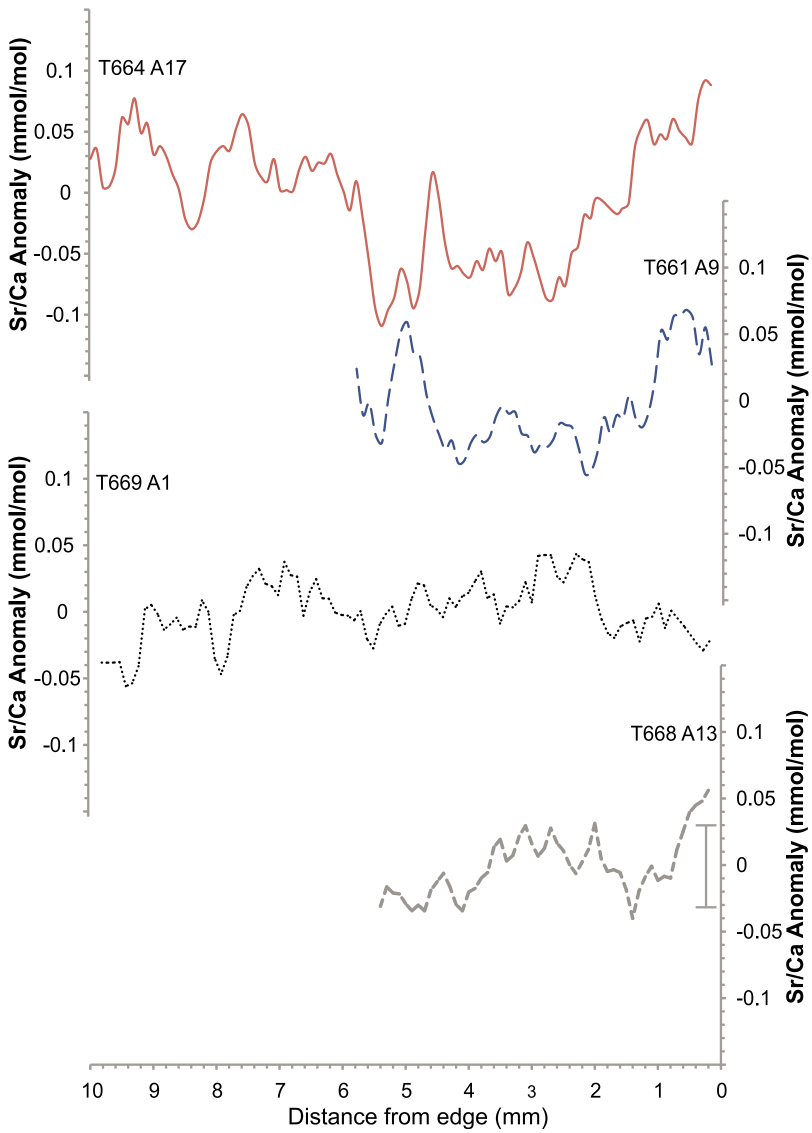

Figure 2. Sr/Ca$_{coral}$ plotted versus distance from margin (edge) of four corals: T664 A17 (1295 m, red line), T661 A9 (792 m, blue dashed line), T669 A1 (2043 m, black dotted line), T668 A13 (2136 m, gray dashed line). All lines reflect a 3-point moving average of individual points (100 μm spacing). Error bar indicates ±0.03 mmol/mol reproducibility of LA-ICP-MS Sr/Ca$_{coral}$ data (0.85–1.05%).

suggests that the Sr/Ca$_{sw}$ composition of NPIW is more variable than that of PDW. This trend is consistent with documented peaks in [Sr] and Sr/Ca$_{sw}$ in intermediate waters, due to the dissolution of Acantharia shells sinking from surface waters [*Brass and Turekian*, 1974; *de Villiers*, 1999; *MacKenzie*, 1964]. The Sr/Ca$_{coral}$ variation likely reflects changes in ambient Sr/Ca$_{SW}$ due to variability in Acantharia flux from the surface ocean and subsequent remineralization of shell celestite at NPIW depths. Alternatively, the Sr/Ca$_{coral}$ record may indicate periodic shoaling of the upper boundary of PDW (lower in Sr/Ca$_{sw}$).

[13] We evaluate this further by analyzing the two shallower corals (792 and 1295 m; within NPIW) in time series. These corals exhibit notable oscillations in Sr/Ca$_{coral}$ over the past 100 years (Figure 3), suggesting a potential link between intermediate water Sr/Ca$_{sw}$ and decadal scale surface water variability. Development of more accurate chronological techniques in bamboo corals would further elucidate the timing relationships between these processes. The wide-ranging impacts of decadal scale climate change have been well documented in the surface ocean and terrestrial environments [*Hare and Mantua*, 2000; *Mantua et al.*, 1997;

Table 5. Statistics for Sr/Ca$_{coral}$ Variability[a]

Sample ID	Depth (m)	Sr/Ca$_{coral}$ Mean	Sr/Ca$_{coral}$ SD	Percentage
T661 A9	792	3.41	0.050	1.47%
T664 A17	1295	3.00	0.060	2.00%
T669 A1	2043	3.04	0.035	1.15%
T668 A13	2136	3.05	0.030	0.98%

[a]Mean, standard deviation and variance expressed as a percentage of mean for Sr/Ca$_{coral}$ ratios. Shallower (NPIW) corals exhibit higher variability than deeper (PDW) corals. Reproducibility of LA-ICP-MS Sr/Ca$_{coral}$ data is 0.85–1.05%.

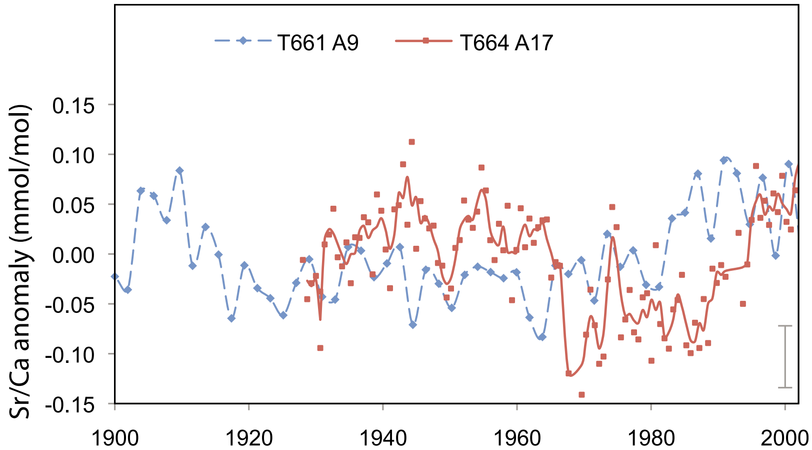

Figure 3. Sr/Ca_{coral} anomaly for T661 A9 (blue dashed line, diamonds) and T664 A17 (solid red line, squares). Data points represent individual analyses. For T661 A9, this generates a sample resolution of ~2 years. To compare the higher resolution (annual) T664 A17 record, the line represents a 3-point moving average for this coral. Error bar (bottom right) indicates ±0.03 mmol/mol reproducibility of LA-ICP-MS Sr/Ca_{coral} data (0.85–1.05%).

Trenberth and Hurrell, 1994]. Although there is little doubt that dramatic surface productivity shifts will influence ecosystems beyond the photic zone, there is limited evidence to date for the penetration of short-term variations in environmental variability to the deep sea [*Corno et al.*, 2007; *Ruhl and Smith*, 2004; *Ruhl et al.*, 2008; *Smith et al.*, 2009; *Wu et al.*, 1999]. Bamboo corals may provide an opportunity to reconstruct such surface-to-deep water linkages.

5. Conclusions

[14] Here we provide evidence that Sr/Ca_{coral} is a proxy for Sr/Ca_{sw}, and that Sr/Ca_{coral} records show significant variability on decadal timescales. These Sr/Ca_{coral} records provide new insight into variations in deep sea Sr/Ca_{sw} shifts, potentially driven by surface water productivity. These findings indicate broad scale shifts in deep ocean Sr/Ca_{sw} content over the past 100 years. These results require a reconsideration of previous paleoceanographic data that assumed stable deep-sea Sr/Ca_{sw} and provide evidence for direct linkages between surface water productivity and alterations to intermediate water geochemistry.

[15] **Acknowledgments.** California seamount sampling and geochemical analyses were supported by NOAA West Coast Polar Regions Research Program (NA030AR4300104 to T.M.H. and H.J.S.) and NSF (OCE 0647872 to T.M.H.). DAC and collection of samples using the R/V *Western Flyer* and ROV *Tiburon* were supported by a grant to MBARI from the David and Lucile Packard Foundation. A portion of this work was performed under the auspices of the U.S. Department of Energy by Lawrence Livermore National Laboratory (contract W-7405-Eng-48) including LLNL IGPP funding (H.J.S. and T.P.G.). We appreciate the technical support of M. Gras-Oqvist, UCD Interdisciplinary Center for Plasma Mass Spectrometry, and staff of LLNL CAMS. This manuscript benefited from suggestions by R. Thresher and two anonymous reviewers, as well as guidance from R. Zahn.

References

Bath, G. E., S. R. Thorrold, C. M. Jones, S. E. Campana, J. W. McLaren, and J. W. H. Lam (2000), Strontium and barium uptake in aragonitic otoliths of marine fish, *Geochim. Cosmochim. Acta*, *64*(10), 1705–1714, doi:10.1016/S0016-7037(99)00419-6.

Bostock, H. C., B. N. Opdyke, and M. J. M. Williams (2010), Characterizing the intermediate depth waters of the Pacific Ocean using $\delta^{13}C$ and other geochemical tracers, *Deep Sea Res., Part I*, *57*, 847–859, doi:10.1016/j.dsr.2010.04.005.

Brass, G. W., and K. K. Turekian (1974), Strontium distribution in GEOSECS oceanic profiles, *Earth Planet. Sci. Lett.*, *23*, 141–148, doi:10.1016/0012-821X(74)90041-7.

Corno, G., D. M. Karl, M. J. Church, R. M. Letelier, R. Lukas, R. R. Bidigare, and M. R. Abbott (2007), Impact of climate forcing on ecosystem processes in the North Pacific Subtropical Gyre, *J. Geophys. Res.*, *112*, C04021, doi:10.1029/2006JC003730.

De Deckker, P. (2004), On the celestite-secreting Acantharia and their effect on seawater strontium to calcium ratios, *Hydrobiologia*, *517*(1–3), 1–13, doi:10.1023/B:HYDR.0000027333.02017.50.

de Villiers, S. (1999), Seawater strontium and Sr/Ca variability in the Atlantic and Pacific oceans, *Earth Planet. Sci. Lett.*, *171*(4), 623–634, doi:10.1016/S0012-821X(99)00174-0.

Hare, S. R., and N. J. Mantua (2000), Empirical evidence for North Pacific regime shifts in 1977 and 1989, *Prog. Oceanogr.*, *47*, 103–145, doi:10.1016/S0079-6611(00)00033-1.

Hill, T. M., H. J. Spero, T. P. Guilderson, M. LaVigne, D. Clague, S. Macalello, and N. Jang (2011), Temperature and vital effect controls on bamboo coral (Isididae) isotope geochemistry: A test of the "lines method", *Geochem. Geophys. Geosyst.*, *12*, Q04008, doi:10.1029/2010GC003443.

Johnson, G. C., and J. M. Toole (1993), Flow of deep and bottom waters in the Pacific at 10N, *Deep Sea Res., Part I*, *40*, 371–394, doi:10.1016/0967-0637(93)90009-R.

LaVigne, M., T. M. Hill, H. J. Spero, and T. P. Guilderson (2011), Bamboo coral Ba/Ca: Calibration of a new deep ocean refractory nutrient proxy, *Earth Planet. Sci. Lett.*, *312*, 506–515, doi:10.1016/j.epsl.2011.10.013.

Levitus, S. (1994), LEVITUS94: World Ocean Atlas 1994, an atlas of objectively analyzed fields of major ocean parameters at the annual, seasonal, and monthly timescales, http://ingrid.ldeo.columbia.edu/SOURCES/.LEVITUS94/, Natl. Oceanogr. Data Cent., Silver Spring, Md.

MacKenzie, F. T. (1964), Strontium content and variable strontium-chlorinity relationship of Sargasso Sea water, *Science*, *146*, 517–518, doi:10.1126/science.146.3643.517.

Mantua, N. J., S. R. Hare, Y. Zhang, J. M. Wallace, and R. C. Francis (1997), A Pacific interdecadal climate oscillation with impacts on salmon production, *Bull. Am. Meteorol. Soc.*, *78*, 1069–1079, doi:10.1175/1520-0477(1997)078<1069:APICOW>2.0.CO;2.

Martin, P. A., D. W. Lea, T. A. Mashiotta, T. Papenfuss, and M. Sarnthein (1999), Variation of foraminiferal Sr/Ca over Quaternary glacial-interglacial cycles: Evidence for changes in mean ocean Sr/Ca?, *Geochem. Geophys. Geosyst.*, *1*(12), 1004, doi:10.1029/1999GC000006.

Michaels, A. F. (1988), Vertical distribution and abundance of Acantharia and their symbionts, *Mar. Biol. Berlin*, *97*, 559–569, doi:10.1007/BF00391052.

Michaels, A. F. (1991), Acantharian abundance and symbiont productivity at the VERTEX seasonal station, *J. Plankton Res.*, *13*(2), 399–418, doi:10.1093/plankt/13.2.399.

Noé, S. U., L. Lembke-Jene, and W.-C. Dullo (2008), Varying growth rates in bamboo corals: Sclerochronology and radiocarbon dating of a mid-Holocene deep water gorgonian skeleton (Keratoisis sp.: Octocorallia) from Chatham Rise (New Zealand), *Facies*, *54*, 151–166, doi:10.1007/s10347-007-0129-x.

Phillis, C. C., D. J. Ostrach, B. L. Ingram, and P. K. Weber (2011), Evaluating otolith Sr/Ca as a tool for reconstructing estuarine habitat use, *Can. J. Fish. Aquat. Sci.*, *68*(2), 360–373, doi:10.1139/F10-152.

Reid, J. L. (1965), *Intermediate Waters of the Pacific Ocean*, *Johns Hopkins Oceanogr. Stud.*, vol. 2, 85 pp., Johns Hopkins Press, Baltimore, Md.

Roark, E. B., T. P. Guilderson, S. Flood-Page, R. B. Dunbar, B. L. Ingram, S. J. Fallon, and M. McCulloch (2005), Radiocarbon-based ages and growth rates of bamboo corals from the Gulf of Alaska, *Geophys. Res. Lett.*, *32*, L04606, doi:10.1029/2004GL021919.

Ruhl, H. A., and K. L. Smith Jr. (2004), Shifts in deep-sea community structure linked to climate and food supply, *Science*, *305*, 513–515, doi:10.1126/science.1099759.

Ruhl, H. A., J. A. Ellena, and K. L. Smith (2008), Connections between climate, food limitation, and carbon cycling in abyssal sediment communities, *Proc. Natl. Acad. Sci. U. S. A.*, *105*(44), 17,006–17,011, doi:10.1073/pnas.0803898105.

Sinclair, D. J., B. Williams, G. Allard, B. Ghaleb, S. Fallon, S. W. Ross, and M. Risk (2011), Reproducibility of trace element profiles in a specimen of deep water Bamboo coral Keratoisis sp, *Geochim. Cosmochim. Acta*, *75*(18), 5101–5121, doi:10.1016/j.gca.2011.05.012.

Smith, K. L., H. A. Ruhl, B. J. Bett, D. S. M. Billett, R. S. Lampitt, and R. S. Kaufmann (2009), Climate, carbon cycling, and deep-ocean ecosystems, *Proc. Natl. Acad. Sci. U. S. A.*, *106*(46), 19,211–19,218, doi:10.1073/pnas.0908322106.

Sosdian, S., D. K. Gentry, C. H. Lear, E. L. Grossman, D. Hicks, and Y. Rosenthal (2006), Strontium to calcium ratios in the marine gastropod Conus ermineus: Growth rate effects and temperature calibration, *Geochem. Geophys. Geosyst.*, *7*, Q11023, doi:10.1029/2005GC001233.

Stoecker, D. K., D. E. Gustafson, and P. G. Verity (1996), Micro- and mesoprotozooplankton at 140 degrees W in the equatorial Pacific: Heterotrophs and mixotrophs, *Aquat. Microb. Ecol.*, *10*(3), 273–282, doi:10.3354/ame010273.

Stoll, H. M., D. P. Schrag, and S. C. Clemens (1999), Are seawater Sr/Ca variations preserved in Quaternary foraminifera?, *Geochim. Cosmochim. Acta*, *63*(21), 3535–3547, doi:10.1016/S0016-7037(99)00129-5.

Stoll, H. M., Y. Rosenthal, and P. Falkowski (2002), Climate proxies from Sr/Ca of coccolith calcite: Calibrations from continuous culture of Emiliania huxleyi, *Geochim. Cosmochim. Acta*, *66*(6), 927–936, doi:10.1016/S0016-7037(01)00836-5.

Stoll, H. M., P. Ziveri, N. Shimizu, M. Conte, and S. Theroux (2007), Relationship between coccolith Sr/Ca ratios and coccolithophore production and export in the Arabian Sea and Sargasso Sea, *Deep Sea Res., Part II*, *54*(5–7), 581–600, doi:10.1016/j.dsr2.2007.01.003.

Strnad, L., V. Ettler, M. Mihaljevic, J. Hladil, and V. Chrastny (2009), Determination of trace elements in calcite using solution and laser ablation ICP-MS: Calibration to NIST SRM Glass and USGS MACS Carbonate, and application to real landfill calcite, *Geostand. Geoanal. Res.*, *33*(3), 347–355, doi:10.1111/j.1751-908X.2009.00010.x.

Stuiver, M., and H. A. Polach (1977), Discussion and reporting of 14C data, *Radiocarbon*, *19*, 355–363.

Talley, L. D. (1988), Potential vorticity distribution in the North Pacific, *J. Phys. Oceanogr.*, *18*, 89–106, doi:10.1175/1520-0485(1988)018<0089:PVDITN>2.0.CO;2.

Talley, L. D. (1993), Distribution and formation of North Pacific Intermediate Water, *J. Phys. Oceanogr.*, *23*, 517–537, doi:10.1175/1520-0485(1993)023<0517:DAFONP>2.0.CO;2.

Thresher, R. E., S. R. Rintoul, J. A. Koslow, C. Weidman, J. F. Adkins, and C. Proctor (2004), Oceanic evidence of climate change in southern Australia over the last three centuries, *Geophys. Res. Lett.*, *31*, L07212, doi:10.1029/2003GL018869.

Thresher, R. E., C. M. MacRae, N. C. Wilson, and S. Fallon (2009), Feasibility of age determination of deep-water bamboo corals (Gorgonacea; Isididae) from annual cycles in skeletal composition, *Deep Sea Res., Part I*, *56*, 442–449, doi:10.1016/j.dsr.2008.10.003.

Thresher, R. E., N. C. Wilson, C. M. MacRae, and H. Neil (2010), Temperature effects on the calcite skeletal composition of deep-water gorgonians (Isididae), *Geochim. Cosmochim. Acta*, *74*, 4655–4670, doi:10.1016/j.gca.2010.05.024.

Tracey, D. M., H. Neil, P. Marriott, A. H. Andrews, G. M. Cailliet, and J. A. Sanchez (2007), Age and growth of two genera of deep-sea bamboo corals (Family Isididae) in New Zealand Waters, *Bull. Mar. Sci.*, *81*(3), 393–408.

Trenberth, K. E., and J. W. Hurrell (1994), DECADAL ATMOSPHERE-OCEAN VARIATIONS IN THE PACIFIC, *Clim. Dyn.*, *9*(6), 303–319, doi:10.1007/BF00204745.

Wu, J. P., S. E. Calvert, C. S. Wong, and F. A. Whitney (1999), Carbon and nitrogen isotopic composition of sedimenting particulate material at Station Papa in the subarctic northeast Pacific, *Deep Sea Res., Part II*, *46*(11–12), 2793–2832, doi:10.1016/S0967-0645(99)00084-3.