Tidal modulation of Sr/Ca ratios in a Pacific reef coral

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[1]   The strontium-to-calcium ratio (Sr/Ca) of reef coral skeleton is an important tool for reconstructing past sea surface temperatures (SSTs). However, the accuracy of paleoSSTs derived from fossil coral Sr/Ca is challenged by evidence that physiological processes influence skeletal chemistry. Here we show that water level variations from tidal forcing are correlated with changes in coral Sr/Ca that cannot be accounted for by changes in SST. Ion microprobe measurements of Sr/Ca ratios in a Pacific *Porites lutea* reveal high-frequency variations at periods of ~6, ~10, and ~25 days. The relationship between Sr/Ca and temperature on these short timescales does not follow trends observed at longer periods, indicating that an additional forcing is required to explain our observations. We demonstrate that Sr/Ca is correlated with both tidal water level variations and SST, and that their contributions to the Sr/Ca content of the skeleton vary as a function of period. We propose that water level influences Sr/Ca indirectly via modulation of photosynthetically-active radiation (PAR) that drives large changes in zooxanthellate photosynthesis.   *INDEX TERMS:* 4267 Oceanography: General: Paleoceanography; 4294 Oceanography: General: Instruments and techniques; 4825 Oceanography: Biological and Chemical: Geochemistry; 4853 Oceanography: Biological and Chemical: Photosynthesis. **Citation:** Cohen, A. L., and R. A. Sohn (2004), Tidal modulation of Sr/Ca ratios in a Pacific reef coral, *Geophys. Res. Lett.*, *31*, L16310, doi:10.1029/2004GL020600.

1.   Introduction

[2]   The strontium to calcium ratio (Sr/Ca) of reef coral skeleton is inversely correlated with sea temperature and is used to reconstruct ocean temperatures during important periods in Earth's climate history [e.g., *Guilderson et al.*, 1994; *Beck et al.*, 1997; *Correge et al.*, 2004]. However, interpretation of paleoSST estimates obtained from coral Sr/Ca is confounded by vital effects, [*Weber*, 1973; *de Villiers et al.*, 1995; *Cohen et al.*, 2001, 2002; *Felis et al.*, 2004] which may be substantial relative to the small temperature dependence of Sr/Ca in experimentally produced aragonite crystals [*Kinsman and Holland*, 1969; *Dietzel et al.*, 2004]. Microscale analyses of coral skeleton reveal significant variability in Sr/Ca on short (<100 μm) skeletal lengthscales, equivalent to a few days of growth. These fluctuations are not observed in coral Sr/Ca records generated using bulk sampling techniques, which are too coarse to resolve subseasonal variability. The apparent heterogeneity in Sr/Ca distribution within coral skeleton has been attributed to variations in calcification rate [*Weber*, 1973], the presence of organic matrix [*Allison*, 1996] and

strontianite [*Greegor et al.*, 1997] and to physiological processes linked to coral spawning [*Meibom et al.*, 2003]. *Cohen et al.* [2001] noted that biweekly oscillations in Sr/Ca of a Pacific *Porites* appeared to match smaller oscillations in the in situ SST record. To better constrain the periodicity and potential causes of high-frequency oscillations in coral skeletal chemistry, we analyzed the Sr/Ca composition of a shallow water *Porites lutea* colony at ~ daily resolution over a 6-month period. A stainline emplaced in the live colony provided constraints on chronology and growth rate. Corresponding in situ daily SST and tidal records were acquired, and the timing and duration of coral spawning events was recorded.

2.   Samples and Analytical Technique

[3]   The coral, 275 mm high, was collected from the lagoon on Johnston Atoll, north central Pacific (6°44.3′N 169°31.8′W) on November 2nd, 1996. The top of the dome lay ~1 m from the sea surface, perpendicularly aligned to the reef substrate. Six months prior to collection (April 25th, 1996), we stained the live colony using Alizarin Red S and placed a temperature logger at its base. A slab cut from the center of the colony revealed the stainline ~4 mm from the surface, indicating an average daily growth rate of 21-μm over the study period. A subsample 5 mm wide by 20 mm long was cut from the fastest growth axis, epoxy-mounted in a 1″-diameter Al ring and final polished with 0.3-μm alumina suspension. A Cameca 3f Ion Microprobe employing a 4 nA O^- primary ion beam accelerated at 12.5 keV sputtered discrete 20-μm diameter spots, i.e., ~ daily sampling resolution, along the length of a single skeletal spine within a corallite from the stainline to the surface (Figure 1). Secondary ion intensities for ^{88}Sr and ^{42}Ca were measured using a −80 eV (±30) energy filter.

3.   Skeletal Microstructure

[4]   *P. lutea* is a massive, long-lived reef coral commonly used for paleoceanographic reconstruction. The porous skeleton is a scaffolding of vertical spines connected by horizontal rungs, the synapticulae (Figure 1a). In our coral sample, the synapticulae are spaced ~260 microns (~12 days) apart, indicating that the rungs formed once a fortnight. Growth of a vertical skeletal rod occurs by initial daily accretion of a calcification center from which emerge bundles of long, thin crystals (Figure 1b). Sr/Ca ratios decrease across the width of the skeletal spine, from the calcification center to the tips of the needles [*Cohen and McConnaughey*, 2003]. Therefore, varying the position of the sample spot within the bundle contributes significant "noise" (random heterogeneity) to a Sr/Ca time series. To avoid this, we sampled each bundle at its base i.e., close to
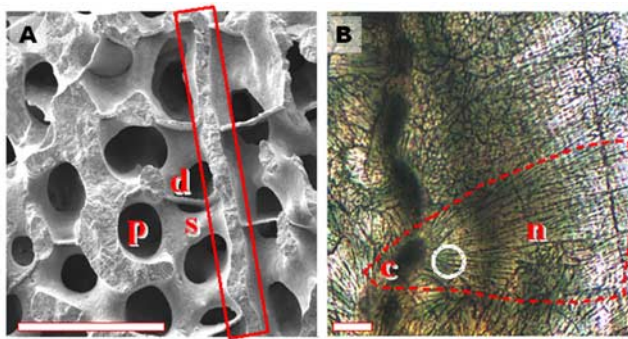
Figure 1. Meso- and ultrastructural features of *Porites* skeleton seen in SEM (A) and thin section (B). In (A) Sr/Ca ratios were measured along the length of a vertical spine (enclosed in red box). Horizontal rungs, synapticulae (s) link adjacent spines creating pore spaces (p). Periodic accretion of fine horizontal sheets, dissepiments (d), provides a seat for the base of the tissue layer. Scale Bar = 0.5 mm. In (B), fine aragonite needles (n) emerge from calcification centers (c) in bundles, enclosed within the dotted line. The white circle indicates size and position of an ion microprobe analysis spot. Scale Bar ∼20-μm.

the calcification center, effectively analyzing each at the same stage of its daily growth cycle (Figure 1b).

4. Results

[5] Sr/Ca ratios decrease from ∼9.40 mmol/mol to ∼8.22 mmol/mol (Figure 2a) as SSTs increase from 25.44°C (May 1st) to the summer maximum of 28.70°C (August 24th) (Figure 2b), consistent with the observed inverse relationship between aragonite Sr/Ca and temperature [*Kinsman and Holland*, 1969; *Dietzel et al.*, 2003]. Large, short-period fluctuations in Sr/Ca are superimposed upon the long-term trend, with largest amplitudes occurring over a six week period from mid-May through mid-July. The recorded SSTs also exhibit high-frequency oscillations superimposed upon the seasonal cycle, but the character of these oscillations differs from those observed in the Sr/Ca record. The amplitude of short-period SST oscillations relative to the seasonal range is much smaller than the Sr/Ca oscillations, and there is no amplification of the short-period SST oscillations from May through July.
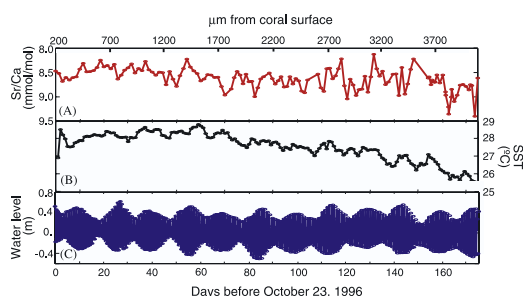
[6] The disparity between the nature of the high-frequency variations in the Sr/Ca and SST data indicates that coral Sr/Ca is responding to another forcing besides temperature. We used NOAA tide gauge data from Johnson Atoll to evaluate the potential influence of water level variations on coral Sr/Ca (Figure 2c). Water level in the lagoon fluctuates with a mean daily range of ∼0.8 m. Large excursions (±0.5 m) occur on 7-day cycles (neap to spring tide) and smaller excursions (±0.1−0.2 m) occur with biweekly periodicity (spring to spring tide) (Figure 2c). We assumed a constant coral extension rate of 21 μm/day to convert sampling distance (μm) to time (days). The Sr/Ca, SST and tidal records were then filtered and normalized to enable direct comparison of signal variability in discrete frequency bands (Figure 3). At the longest periods resolvable with our data (∼50 days), the Sr/Ca record exhibits characteristics of both SST and tide, with a seasonal envelope apparent in the SST record and a distinct "double hump" apparent in the tidal record (Figure 3a). At shorter periods (4−50 days), the Sr/Ca data exhibit characteristics of both SST and tidal records (Figures 3b and 3c).

[7] We conducted a spectral analysis of the Sr/Ca, SST and tide gauge data to quantify the statistical relationships amongst them, and to investigate the potential role of tidal forcing in modulating coral Sr/Ca (Figure 4). The normalized power spectra reveal subannual peaks in the Sr/Ca data centered on ∼6, ∼10, ∼25, and ∼50 days (Figure 4). The relative power (i.e., variance) in the Sr/Ca data is greater than both the SST and the tidal signals at short periods (<40 days), but many of the Sr/Ca spectral peaks are mimicked in the SST and tidal spectra.

[8] The statistical correlation amongst the three datasets was assessed using a coherency analysis applied over a range of possible growth rates centered about the average value of 21-μm/day (Figure 5). SST and water level are both correlated with Sr/Ca, but the correlations are a function of forcing period. At subannual periods >50 days, Sr/Ca correlates with both SST and water level (Figure 5a), with tidal coherencies consistently exceeding temperature coherencies. At ∼28 day periods, Sr/Ca correlates with temperature, but not strongly with tide (Figure 5b). At 6−7 day periods, Sr/Ca is correlated with water level but not
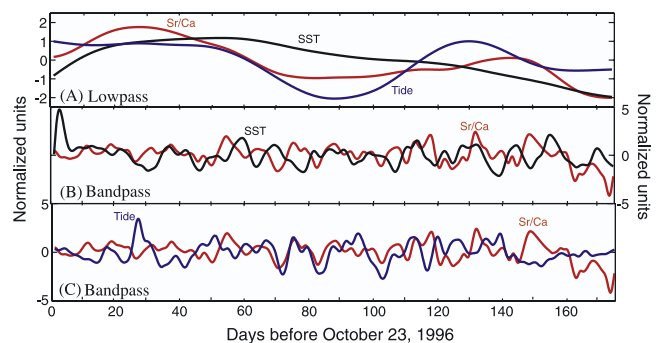

Figure 2. Raw data used in this study. (A) Sr/Ca (open red circles) as a function of distance from the coral surface and time using coral growth rate = 21 μm/day. (B) In situ SST record. (C) Water level variations in the Johnston Atoll lagoon (data from http://www.co-ops.nos.noaa.gov/).

Figure 3. Filtered and normalized (zero mean, unit variance) data records. In (A) a low-pass filter (4-pole, zero-phase, Butterworth digital filter with a corner period of 50 days) is applied. In (B,C), a band-pass filter (4-pole, zero-phase, Butterworth digital filter with corner periods of 4 and 50 days) is applied.
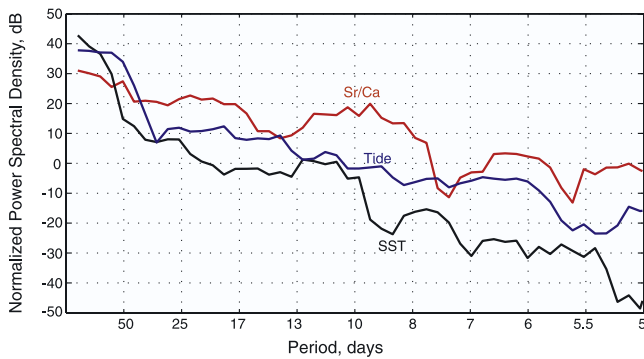
Figure 4. Power spectra of low-pass filtered (4-pole, zero-phase, Butterworth digital filter with a corner period of 4 days) and normalized data. Spectral estimates formed using the multi-taper method with a time-bandwidth product of 2. The x-axis is plotted on a non-linear scale (1/frequency) enabling inspection of high-frequency spectral structure.

with temperature. Short period coherency estimates (e.g., weekly periods) are statistically robust but sensitive to growth rate (Figure 5c). Conversely, coherency estimates at >biweekly periods are insensitive to growth rate but have larger formal statistical uncertainty due to the smaller effective sample size.

[9] The transfer function between Sr/Ca, SST and tides was quantified as a function of period. At >50 day periods, Sr/Ca varies as 0.1 mmol/mol/°C and 3 mmol/mol/m of water. At 6–7 day periods Sr/Ca varies as 4–8 mmol/mol/m of water, and at ~28 day periods, Sr/Ca varies as ~0.35 mmol/mol/°C. Interpretation of our statistical results must consider the short duration of the record and the potential for small growth rate changes within the study period. Nevertheless, the following results are considered robust: (1) long-period, subannual Sr/Ca variations correlate with both SST and water level, (2) short-period (6–7 day) Sr/Ca oscillations cannot be explained by temperature but appear consistent with tidal forcing.

5. Discussion

[10] Our data suggest that coral Sr/Ca is modulated by water level as well as water temperature. Inorganic aragonite precipitation experiments demonstrate a small but direct temperature dependence in the exchange of Sr/Ca between seawater and aragonite [*Kinsman and Holland*, 1969; *Dietzel et al.*, 2003]. We propose that water level variations from tidal forcing affect coral Sr/Ca indirectly by modulating zooxanthellate photosynthesis. During periods of active photosynthesis, symbiotic corals have lower skeletal Sr/Ca ratios than asymbiotic corals, at the same temperature [*Cohen et al.*, 2002]. This may occur because selective uptake of Ca^{2+} relative to Sr^{2+} by the calcification enzyme Ca^{2+}-ATPase is enhanced during periods of maximum photosynthesis [*Ferrier-Pagès et al.*, 2002], depleting $[Sr^{2+}]$ relative to $[Ca^{2+}]$ in the calcifying fluid. Thus, skeleton accreted when photosynthesis and calcification rates are high, has lower Sr/Ca ratios [*Cohen and McConnaughey*, 2003].

[11] Zooxanthellate photosynthesis is sensitive to tidal forcing because the amount of photosynthetically-active radiation (PAR) received at the colony surface is modulated

by water level [*Anthony and Hoegh-Guldberg*, 2003]. Changes in water level during the spring-neap, spring-to-spring and lunar tidal cycles cause weekly, biweekly and monthly fluctuations in PAR received by corals at shallow and intermediate depths, and result in corresponding fluctuations in zooxanthellae photosynthesis [*Anthony and Hoegh-Guldberg*, 2003]. Sr/Ca ratios in this coral correlate inversely with water level implying that maximum photosynthesis occurs at high tide when PAR received by the coral is lower than at low tide. A negative correlation between irradiance and photosynthesis suggests that coral zooxanthellae in this shallow water environment experience dynamic photoinhibition, a temporary reduction in photosynthetic efficiency caused by excessive UV exposure [*Vincent and Neale*, 2000]. The exaggerated amplitude of the Sr/Ca oscillations observed from mid-May through mid-July may reflect maximum net photosynthesis obtained during neap and spring tide in early summer when optimal irradiance and daylength, higher than average water level, and cool water temperatures combine to prevent photoinhibition and promote optimal conditions for symbiont photosynthesis, as observed by *Tougas* [2001] for Floridian *Montastrea annularis*.

[12] Monthly oscillations in Sr/Ca of a Kenyan *Porites* have been attributed to metabolic changes associated with coral spawning [*Meibom et al.*, 2003]. Monthly Sr/Ca oscillations were detected in our coral but the spectral power at weekly and biweekly periods is much stronger. Furthermore, spawning events on Johnston Atoll occur sporadically over a two month period from early May through late June (L. Hayes, US Fish and Wildlife, Johnston Atoll, personal communication, 2003) and are therefore unlikely to account for the high frequency Sr/Ca variability in this coral observed throughout the 6 month study period.

[13] Photosynthesis and calcification are tightly coupled in zooxanthellate scleractinian corals [*Gattuso et al.*, 1999]. Monthly and submonthly variations in calcification rate accompany formation of dissepiments and fine (subseasonal) density bands [*Buddemeier*, 1974; *Barnes and Lough*, 1993]. Synapticulae in our coral form with approximate
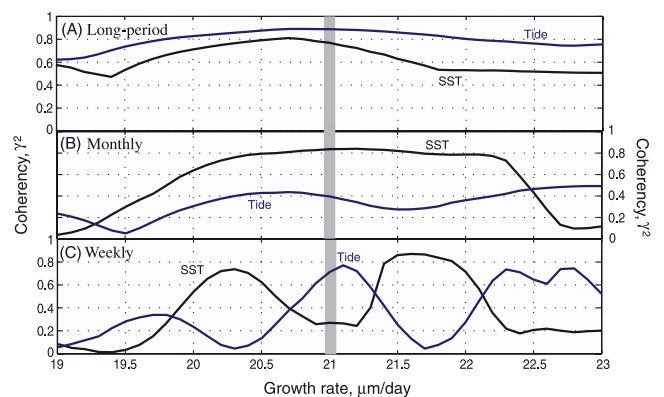

Figure 5. Coherency results for Sr/Ca vs SST (black) and Sr/Ca vs water level (blue) for a range of growth rates (vertical gray bar = 21 μm/day). (A) Maximum coherency at periods >50 days. (B) Maximum coherency at ~28 day periods. (C) Maximum coherency at 6–7 day periods. Coherency estimates calculated using multi-taper spectral methods with a time-bandwidth product of 2.

12 day periodicity, coincident with the 9–13 day peak in the Sr/Ca spectral power. Formation of synapticulae probably signals an overall increase in colony calcification rate and may account for the strong biweekly periodicity in Sr/Ca. Our stochastic analyses did not reveal a strong correlation amongst Sr/Ca, tide and SST on biweekly timescales, suggesting that synapticulae formation may not be responding to either of these forcings. However, more robust constraints on day-to-day growth rate variations will be required to test this assertion.

6. Conclusion

[14] We have identified water level variations from tidal forcing as a potential source of non-temperature dependent Sr/Ca variability in the skeleton of a Pacific reef coral. Our analyses suggest that SST is the main forcing of Sr/Ca over the annual cycle because the tidal contribution is small at these periods. However, water level variations may affect Sr/Ca-derived SST estimates because our model implies that coral Sr/Ca is sensitive to the distance of the top of the colony from the sea surface. Thus, coral colonies collected at different depths [*Weber*, 1973], massive colonies that grow and increase in height, and coral communities surviving sea level changes may reflect these changes in their Sr/Ca ratios. With further investigation and considerations of photoacclimation, sea level forcing of coral Sr/Ca may provide a valuable new proxy for paleoclimate reconstructions.

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