

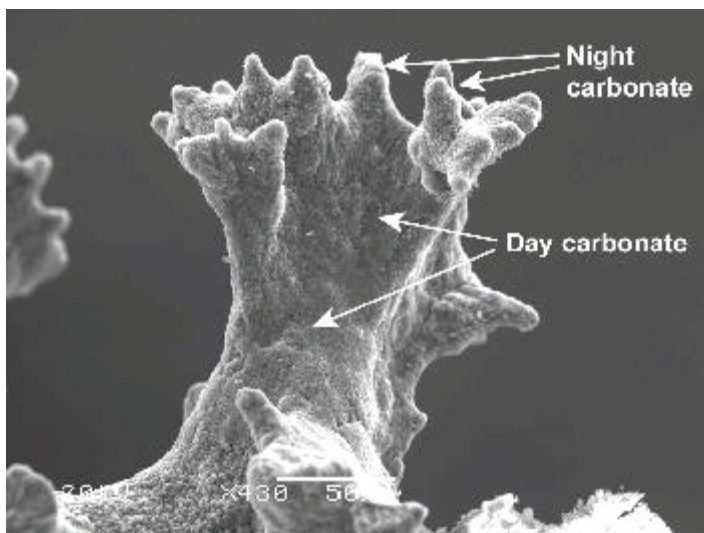
Sr/Ca-SST equations in relation to skeletal architecture in a *Porites* coral from Hawaii

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Introduction

Tropical coral skeletons indicate great promise as proxies of past sea surface temperatures (SSTs) as the geochemistry of the skeleton may encode the environment at the time of skeletal deposition. For example, the substitution of Sr for Ca in aragonite is temperature dependent and the Sr/Ca ratios of fossil coral skeletons have been used as indicators of past SSTs. However Sr/Ca exhibits geochemical heterogeneity on a small spatial scale (<100 μm) that does not reflect variations in SST or chemistry (Allison, 1996). Skeletal Sr/Ca is affected by variations in skeletal calcification rate that may be dependent on the photosynthetic activity of the symbiotic algae (zooxanthellae) in the coral tissue. The skeleton deposited at night may be unaffected by these variations and may be a more reliable indicator of SST (Cohen *et al.* 2001).

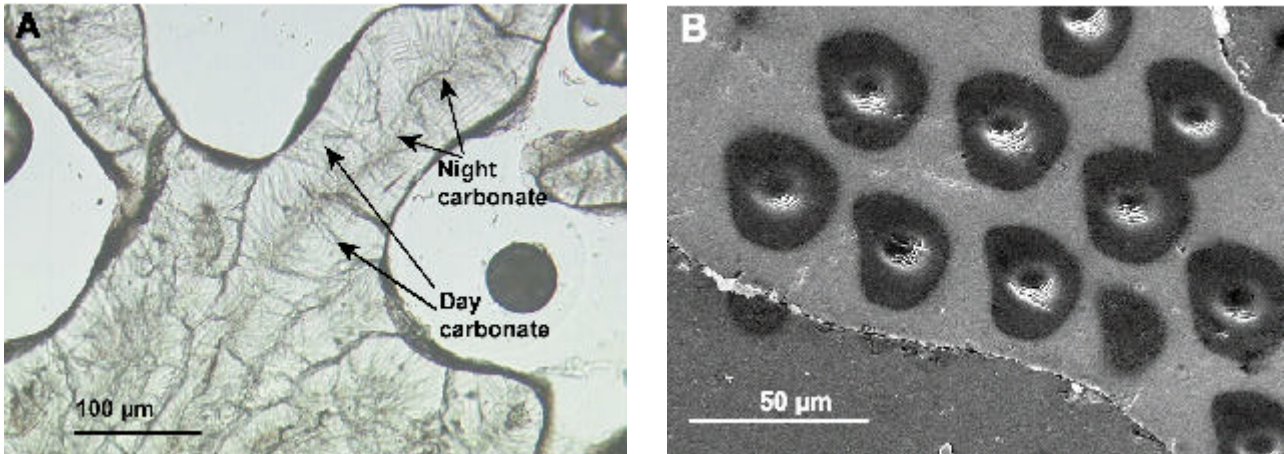


Coral calcification follows a diurnal pattern with large variations in calcification and skeletal extension rates, associated with differences in crystal shape and deposition site. During the night submicron crystals are deposited at the axial spines of the skeleton to form centres of calcification while, during the day, larger needle shaped crystals are deposited over the remaining surfaces to form fasciculi.

Methods

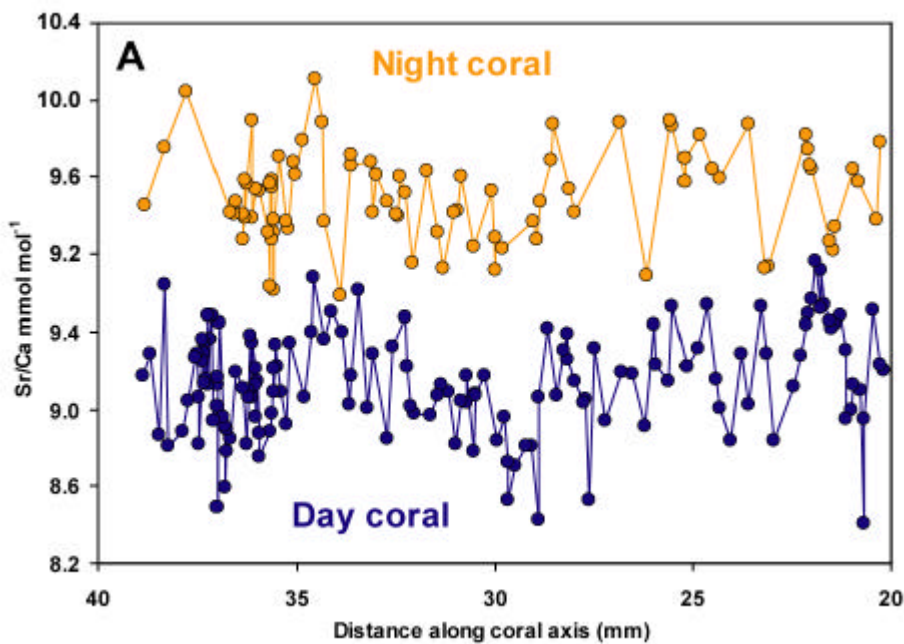
The high spatial resolution of the ion microprobe allows the analysis of day and night structures separately. These areas can be identified in thin section. We used a $\sim 10 \mu\text{m}$ diameter analysis spot to construct records of Sr/Ca across day and night carbonate of an ~ 2 year transect of a *Porites lobata* coral skeleton from Lanikai, Oahu, Hawaii. Instrument conditions: primary beam current = 6nA, energy offset = 75eV, imaged field = 25 μm . We used a pre-analysis burn-in time of 3 minutes to remove surface contamination. Each analysis was the sum of ten cycles and for each cycle we collected secondary ions at masses

^{44}Ca (counting time 2 s) and ^{88}Sr (counting time 4 s). Count rates were approximately 66000 cps and 24000 cps respectively. The total time per analysis (including other isotopes not reported here) was 6 minutes. Measurement precision is $\sim 0.2\%$ 2s for Sr/Ca. The relative ion yield of Sr to Ca was estimated after multiple analyses on the carbonate standard, OKA.

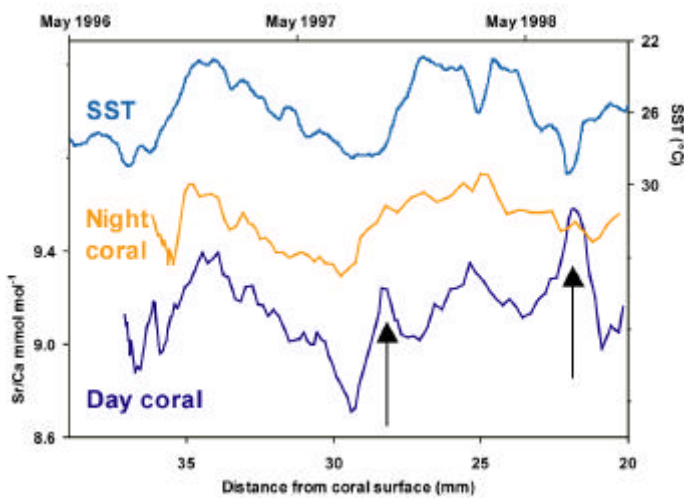


A: Carbonate deposited during the day and night can be readily identified in thin section.
 B: The ion probe burn marks here have a diameter of $\sim 25\ \mu\text{m}$. A collimating aperture was inserted between the sample and the mass spectrometer to ensure that secondary ions were collected from the central $\sim 10\ \mu\text{m}$.

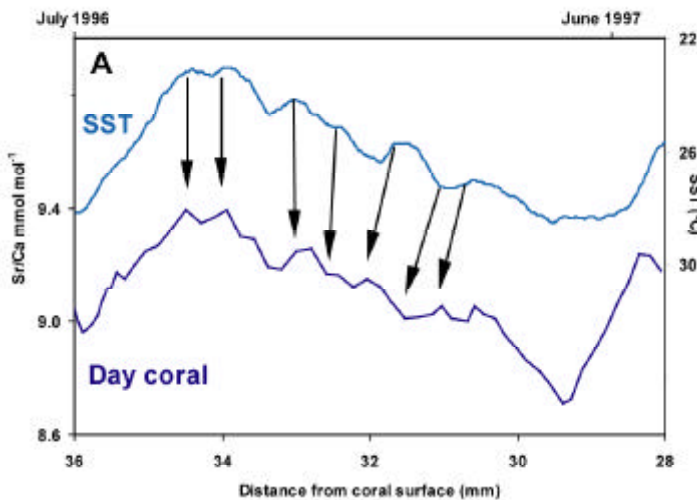
Results



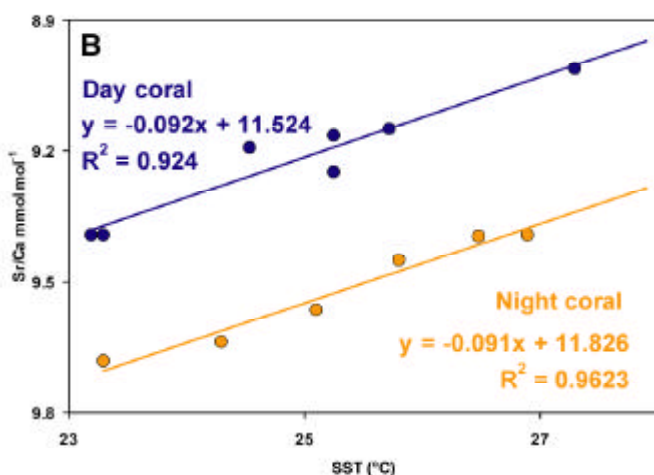
Both day and night profiles exhibit large Sr/Ca heterogeneity. This is not temperature dependent, but probably caused by short term (daily/weekly) variations in skeletal precipitation rate which occur during the day and night (e.g. Marubini et al. 2001, Vago et al., 1997).



Averaging multiple analyses can smooth these variations so that a Sr/Ca- SST signal can be resolved. From July 1996 to July 1997 the Sr/Ca of both day and night carbonate is in good agreement with SST data but in August 1996 and 1997 high Sr/Ca ratios are deposited which do not reflect SST. At these times, SSTs exceed the optimum limits of the coral, the coral becomes stressed and skeletal precipitation rate is reduced (Houck *et al.*, 1987) resulting in an increase in skeletal Sr/Ca.



We matched multiple points in the seasonal Sr/Ca and SST profiles, outside the temperature range causing thermal stress, for day carbonate and night carbonate (not shown) to calculate the Sr/Ca-SST relationship for this coral. Sr/Ca and SST oscillations are matched for temperatures below the thermal stress threshold (~27°C) for day carbonate. Night carbonate is not shown



The slopes of the Sr/Ca-SST relationships for day and night carbonate are similar and correspond to a change of Sr/Ca of -0.092 and -0.091 mmol mol⁻¹ per °C respectively. The slopes of the Sr/Ca-SST relationships reported in this study are larger than previous estimates. Many coral Sr/Ca-SST relationships have been calculated by matching maxima and minima Sr/Ca and SST (e.g. Gagan *et al.*, 1998). However it is clear from this coral that minimum Sr/Ca ratios are not always deposited in response to maximum SSTs.

Conclusions

Both night and day carbonate are affected by kinetic processes such as precipitation rate. Temperature affects the Sr/Ca of day and night carbonate in a similar manner and there are similar challenges in reconstructing SST records from both materials. The annual SST signal in the skeleton can be overwritten when SSTs exceed an optimum level and the coral is stressed. Other estimates of Sr/Ca-SST relationships may underestimate the sensitivity of Sr/Ca to temperature. The use of these Sr/Ca-SST equations may result in underestimates of past seawater temperatures i.e. past SSTs, predicted from coral records, may have been warmer than previously thought.

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