molecule diffuses toward the step edges at RT, it reshapes the fluctuating Cu step adatoms into the tooth-like nanostructures reported above. It is favorable for the Lander to anchor to the nanostructure at the step edge, because the gain in energy by adsorbing the molecule on the "tooth" relative to the flat terrace is higher than the energy required for creating the tooth (*35*). The dimension of the board and leg fits such that two atomic rows can be accommodated between the legs under the board. This leads to a favorable interaction between the π-system and the Cu atoms underneath. The dimensions and shape of the molecule form a perfect template for the double row of Cu atoms. The nanostructure can often extend further than the length of the molecule. This action takes place in the direction perpendicular to the steps (i.e., the close-packed direction), which is the favored direction for diffusion on Cu(110).

Upon adsorption of the molecules at LT (150 K), no restructuring of the Cu step edges is observed, and the molecules simply anchor to a step edge. At LT, the mobility of Cu kink atoms at the step edge is not high enough for the template to be effective. We can thus conclude that the process of step restructuring is thermally activated.

In conclusion, we have shown by STM manipulation that the Lander molecule locally restructures monoatomic steps, acting as a pinning center for step edge fluctuations on the Cu(110) surface. The Lander acts as a molecular template, reshaping portions of step edges into metallic nanostructures that are two atomic rows wide. Using appropriately designed molecules, this points to a new self-fabrication process at the nanoscale for integrated nanoelectronics.

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31. To ascertain that the STM tip did not influence the conformation of the molecules during the manipulation process, we checked the internal distances of a great number of molecules (>100) lying on bare terraces. The values found are consistent with the ones obtained from manipulated molecules, and we therefore rule out the possibility that the conformational change may be induced by the STM tip.
32. Our ESQC routine is based on the calculation of the full scattering matrix of the STM tunnel junction. The description of this junction encompasses the surface, the adsorbate, the tip apex, and both the bulk material supporting the tip apex and the surface. Whatever the tip apex position is, 695 molecular orbitals are used to describe the electronic properties of the junction with the Lander positioned under the tip apex. The surface atoms and the Lander are described taking into account all valence molecular orbitals. Electronic interactions inside the junction are calculated using a semi-empirical Extended Hückel approximation with a double zeta basis set, in order to properly reproduce the tip apex wave function in space away from the tip apex end atom. The molecular mechanics routine used to optimize the Lander's geometry in the tunnel junction is a standard MM2 routine with a generalized potential for surface metal atoms.
33. A detailed analysis of the STM images reveals an asymmetry in the relative apparent height of the four lobes, i.e., the lobes R, R′ are imaged 0.03 nm higher than the lobes S, S′. From the calculations, we infer that the two smaller lobes (S, S′ in Fig. 1, B and C) are due each to a tunneling path through one leg only, whereas the two larger lobes (R, R′ in Fig. 1, B and C) are due to a more complete tunneling path which forms by a combination of tunneling channels building up through the two legs on the same side of the Lander.
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35. Effective Medium Theory calculations performed as in (*7*) yield an energy of 0.28 eV for the restructuring process at the step edge.
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The Effect of Algal Symbionts on the Accuracy of Sr/Ca Paleotemperatures from Coral

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The strontium-to-calcium ratio (Sr/Ca) of reef coral skeleton is commonly used as a paleothermometer to estimate sea surface temperatures (SSTs) at crucial times in Earth's climate history. However, these estimates are disputed, because uptake of Sr into coral skeleton is thought to be affected by algal symbionts (zooxanthellae) living in the host tissue. Here, we show that significant distortion of the Sr/Ca temperature record in coral skeleton occurs in the presence of algal symbionts. Seasonally resolved Sr/Ca in coral without symbionts reflects local SSTs with a temperature sensitivity equivalent to that of laboratory aragonite precipitated at equilibrium and the nighttime skeletal deposits of symbiotic reef corals. However, up to 65% of the Sr/Ca variability in symbiotic skeleton is related to symbiont activity and does not reflect water temperature.

Accurate estimates of past ocean temperature are key to establishing the sensitivity of the tropics to global climate change (*1–4*). One of the principal techniques used to derive past SSTs is the measurement of Sr/Ca ratios in the aragonite skeleton of massive reef corals (*5–8*). The technique is based on an inverse correlation between temperature and Sr/Ca in living corals that is applied to ancient specimens to reconstruct surface temperatures of past oceans. High measurement precision (*8*) and rapid sample throughput (*9*) afforded by recent technological advances have increased the appeal and utility of the Sr/Ca thermometer. Despite its wide application, paleotemperature estimates derived from coral Sr/Ca remain controversial (*10, 11*). At least nine different Sr/Ca paleotemperature equations have been published for the massive reef coral *Porites*. Among them, a Sr/Ca value of 9 mmol/mol yields a range of SSTs from 22.5°C through 28°C (*8, 12–19*). There are

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several indications that the presence of algal symbionts in reef coral tissue influences the Sr/Ca content of the coral skeleton. The temperature dependence of Sr/Ca in symbiotic reef coral aragonite is double that of Sr/Ca in laboratory aragonite precipitated at equilibrium (*20*); corals with symbionts have generally lower Sr/Ca ratios than do asymbiotic corals at the same temperature (*21*), and Sr/Ca in daytime crystals accreted during peak symbiont photosynthesis by the tropical reef coral *Porites* is five times more sensitive to changes in water temperature than is Sr/Ca in nighttime crystals accreted in the absence of direct symbiont activity (*22*). The important question for paleoceanography is the extent to which the accuracy of coral Sr/Ca-derived SSTs is compromised by the activity of algal symbionts in coral tissue. Here, we show that the temperature-dependence of Sr/Ca in the skeleton of symbiotic corals is masked by a larger signal associated with symbiont photosynthesis. Up to 65% of the Sr/Ca variability occurs independently of changes in water temperature. By contrast, the uptake of Sr/Ca by conspecifics without algal symbionts is directly temperature-dependent and preserves a more reliable record of SST variability.

Fig. 1. *Astrangia poculata* skeleton mounted, polished, and gold-coated for Sr/Ca analyses. Ion microprobe sample spots (s) along outer calical wall (cw) follow the trail of upward skeletal growth indicated by the shallow, discontinuous pits of centers of calcification (p). Inset: A colony is sectioned to expose the calical walls (dashed line) and interior skeletal elements. The location of ion microprobe analyses, from the base to the tip of the calical wall, is indicated by the arrow.

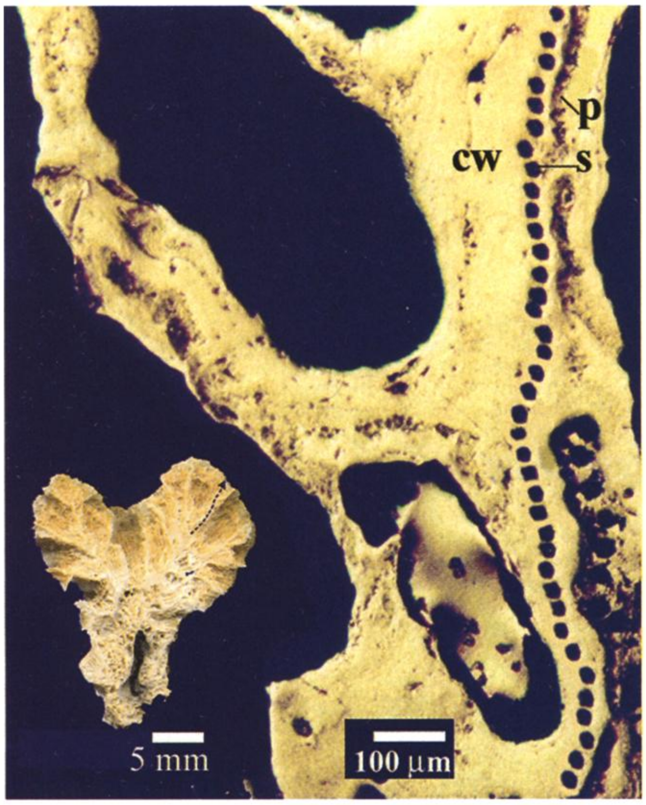
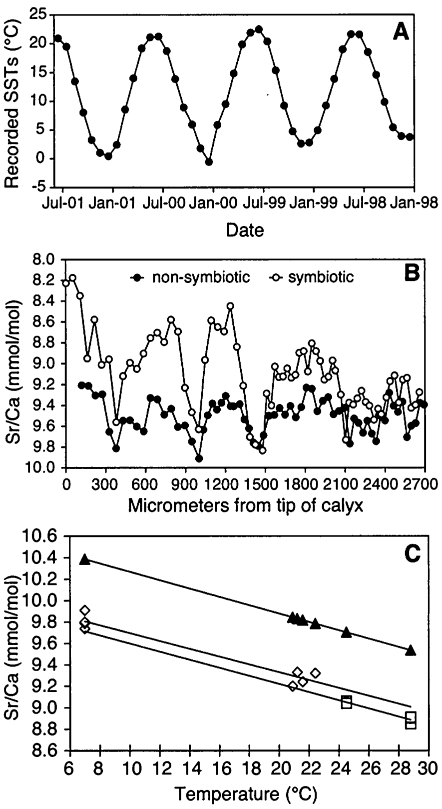


Fig. 2. (**A**) Average monthly SSTs at 12 ft (4 m) depth in the Woods Hole harbor between January 1998 and July 2001. Temperatures were recorded at this site every hour. They show an annual SST range of 25°C and an overall decrease of 0.5°C since the start of the record. (**B**) Life history Sr/Ca profiles from symbiotic (open circles) and asymbiotic (solid circles) skeleton of *Astrangia poculata* colonies collected in Woods Hole in July 2001. Note that Sr/Ca decreases up the *y* axis. Sr/Ca in the most recently deposited skeleton of both corallites (at 0 mm) is at the low end of the annual cycle, in agreement with the expected inverse Sr/Ca-SST correlation. Skeletal Sr/Ca in the first year of life is the same in both samples, but the similarities decrease as the corallites mature, a divergence caused by a progressive decrease in summertime Sr/Ca in the symbiotic skeleton. During summer 2001, Sr/Ca values in the symbiotic skeleton are 65% lower than they are in the asymbiotic skeleton. The corals are exposed to identical environmental conditions; therefore, this difference reflects the impact of symbiont activity on Sr/Ca in the symbiotic coral skeleton. (**C**) The Sr/Ca-SST relationship in asymbiotic *Astrangia* skeleton (◇ = −0.036x + 10.065) is compared with nighttime skeleton of the tropical reef coral *Porites* (□ = −0.038x + 9.9806) and inorganic aragonite precipitated at equilibrium (▲ = −0.039x + 10.66). The slope of the regression equations, indicative of the temperature sensitivity of Sr/Ca uptake into the coral skeleton, are similar for all three precipitates (−0.036, −0.038, and −0.039, respectively). This agreement establishes temperature as the primary control of Sr/Ca in the asymbiotic skeleton.



Astrangia poculata (*23*) is an ahermatypic colonial scleractinian endemic in cool New England waters, where it survives the annual temperature range of –2°C through 23°C (*24*). Although members of the genus *Astrangia* are true corals and co-occur with hermatypic species in warm tropical reef waters (*25*), *A. poculata* is unusual in that colonies occur naturally with and without zooxanthellae (*26–29*). The uniform brown color of symbiont-hosting colonies reflects cellular densities of algae as high as those encountered in tropical reef corals. By comparison, absence of algae from the tissue of asymbiotic colonies is reflected by complete lack of tissue pigmentation (*28, 29*). To examine the effect of symbiosis on coral Sr/Ca, we constructed seasonally-resolved Sr/Ca time series along the calical wall of one symbiotic and one asymbiotic *A. poculata* corallite (Fig. 1) and compared these against a 4-year record of in situ SSTs (Fig. 2A).

Brown and white colonies of equivalent size were collected on snorkel from wooden pilings a few feet beneath the sea surface in the Woods Hole, MA, harbor. Colonies are 3 to 7 cm high, elongate, and contain 100 to 150 corallites with cup-shaped calices, 1 to 7 mm in diameter. We cut through each colony along the growth axis, exposing the calical walls and narrow septa within. Using secondary ion mass spectrometry (SIMS) techniques with a Cameca IMS 3f ion microprobe (*30*), we measured skeletal Sr/Ca at 40-μm intervals from the base to the tip of the calical walls, a distance of 2700 μm. The spatial resolution afforded by the microbeam analysis technique enabled us to avoid the thickened edges of the wall and was crucial to resolving seasonal Sr/Ca variability in slow-growing species.

We focused the O-primary ion beam on crystal bundles close to centers of calcification (*22*), sputtering a sequence of discrete spots 20 μm across and <5 μm deep. Both symbiotic and asymbiotic profiles show strong, covarying Sr/Ca cycles ~600 μm long (Fig. 2B). These are likely to be annual. Low Sr/Ca values at the tips of the calical walls of both colonies correspond to high summer SSTs at the time of collection (July 2001). The number of Sr/Ca cycles indicates a life-span of about 4.5 years for each corallite. Their asymmetric shape, with long, flat summers and short, sharp winters reflects skeletal extension that is strongly seasonal and fastest in the summer.

In the first year of life, mean skeletal Sr/Ca and the annual range of Sr/Ca variability is similar in both specimens. On the basis of laboratory experiments showing active calcification by this species above water temperatures of 6.5°C (*28*, *29*), we calculated the temperature-dependence of Sr/Ca uptake in the young corallites to be −0.036 mmol/mol per °C, which is comparable with abiotic aragonite precipitated close to equilibrium (−0.039 mmol/mol per °C) (*20*) and the nighttime skeletal deposits of symbiotic reef corals, which are accreted in the absence of direct symbiont activity (−0.038 mmol/mol per °C) (*22*) (Fig. 2C). Figure 2B also shows that Sr/Ca in the asymbiotic corallite maintains this level of sensitivity to seasonal and interannual SST fluctuations throughout its life. A slight increase (0.02 mmol/mol) in skeletal Sr/Ca between 1998 and 2001 corresponds to a decrease of ~0.5°C in recorded SSTs over the same time period (Fig. 2, A and B). The correspondence with inorganic aragonite and the correlation with recorded SSTs establishes that asymbiotic Sr/Ca is primarily controlled by temperature.

On the contrary, Sr/Ca in the symbiotic corallite oscillates with much greater amplitude, and water temperature is clearly not the primary control. The interannual Sr/Ca variability is dominated by a strong ontogenetic trend that is unrelated to the recorded SSTs. The increase in amplitude of successive annual Sr/Ca cycles is caused by a decrease in the summertime Sr/Ca values of each successive year, not the wintertime values. As a result, symbiotic Sr/Ca indicates an apparent warming of Woods Hole SSTs in excess of 6°C between 1998 and 2001. Actual temperatures at the study site decreased by 0.5°C over this time period (Fig. 2A).

The difference in amplitude between symbiotic and asymbiotic Sr/Ca cycles is greatest in the summertime, when the rate of photosynthesis by symbiotic algae in the polyparium is highest (*29*). On the other hand, the difference in Sr/Ca between the two corallites is smallest in the wintertime, when the rate of algal photosynthesis in the symbiotic corallite is close to zero (*29*). A similar relationship is observed for the tropical symbiotic reef coral *Porites* (*22*). The largest difference in the Sr/Ca content of day and nighttime crystals occurs in the summertime, whereas Sr/Ca in both crystal types are similar in the wintertime. These observations provide strong support for a causal relationship between symbiont photosynthesis and Sr/Ca in coral skeleton. Experimental results show that calcium deposition into the skeleton of the symbiotic coral *Galaxea fascicularis* is enhanced relative to Sr deposition during active symbiont photosynthesis (*31*). This observation may explain why the ratio of Sr to Ca in *Astrangia* skeleton decreases with the presence and enhanced summertime activity of algal symbionts.

Increased water temperature and increased symbiont photosynthesis both cause a decrease in the relative amount of Sr incorporated into the growing skeleton. The exaggerated seasonality exhibited by Sr/Ca cycles in the symbiotic corallite is considered to be the sum of these two effects. Therefore, the relative contribution of symbiosis can be calculated from the difference in summertime Sr/Ca between the symbiotic and asymbiotic corallites. In the first summer (1997), the difference was almost negligible; however, in the second summer, Sr uptake by the symbiotic corallite was 40% lower than the asymbiotic corallite, and by the fifth summer it was 65% lower. At this point, the apparent temperature-dependence of Sr/Ca uptake by the symbiotic corallite is 0.087 mmol/mol per °C, matching that of tropical symbiotic reef corals (*14*–*18*). However, only 35% of this is temperature driven.

The ontogenetic trend observed in the symbiotic corallite is proportional to the surface area of the calyx exposed to sunlight. A plausible explanation for the trend is that the photosynthetic capacity of the symbiotic polyparium increases over the first 5 years of the creatures' life, probably due to an increase in algal density with expanding calical surface area (*32*). Furthermore, the agreement between Sr/Ca cycles in the symbiotic and asymbiotic corallites in the first year may reflect the initial absence of symbiotic algae from both.

It is concluded that Sr/Ca in the skeleton of asymbiotic *A. poculata* is temperature-dependent, whereas Sr/Ca in symbiotic skeleton is strongly influenced by the activity of algal symbionts in the coral tissue. The degree to which symbiosis affects Sr/Ca is neither constant nor predictable. Although skeletal Sr/Ca in symbiotic colonies fluctuates seasonally and in phase with seasonal SSTs, our study shows that up to 65% of the signal is contributed by processes that are internal to the animal and independent of temperature. On the contrary, the Sr/Ca content of corallites without algal symbionts reflects the recorded interannual temperature variability. The implication is that the Sr/Ca ratio of coral skeleton is a reliable gauge of SST variability, but only when applied to skeleton that is accreted in the absence of direct symbiont activity. Our data indicate that Sr/Ca of asymbiotic species and the nighttime skeletal accretions of symbiotic reef corals should be measured for accurate estimates of past SSTs.

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