than, that of some framework corals (for example, *Montastrea annulares*), the conclusions made for *Galaxea* should be equally valid for at least those same corals. If this is so, the comparison with the azooxanthellate coral *Tubastrea* should also be valid.

While my results are from experiments on "one species each" (hermatype and ahermatype), rather than two of each (the third species were hydrozoans, not scleractinian corals), as in Goreau's paper of 1961 (*2*), they are statistically documented with respect to replication. I compared polyps with polyps of similar size, not polyps with colonies, or colonies with colonies of different polyp sizes and unspecified dimensions, as did Goreau (*2*).

With regard to calcification rates, *Acropora pulchra* was shown to calcify faster than *Tubastrea micrantha* (9). However, if values for *Tubastrea micrantha* are converted from protein to nitrogen units by assuming that the nitrogen content of protein is 16% (*3*), then a calcification rate of 104 μg of calcium per milligram of nitrogen per hour is obtained, which compares well with the values given for *Acropora cervicornis* by Goreau and Goreau (*4*) (61 to 74 μg of calcium per milligram of nitrogen per hour) and Goreau (*5*) (63 to 134 μg of calcium per milligram of nitrogen per hour). If the methods are sufficiently reproducible to permit comparisons, then the comparisons suggest that the azooxanthellate *T. micrantha* calcifies at rates similar to those of the fast growing zooxanthellate *A. cervicornis* [which itself calcifies at rates up to 11 times faster than other zooxanthellate corals (*4*)]. Contrary to being found in "highly protected habitats," *T. micrantha* "is designed well to withstand hydrodynamic attacks and to colonize a current exposed habitat" (*10*).

Goreau *et al.* state that "Marshall's conclusions result apparently in part from inappropriate normalization of his ^{45}Ca uptake data by the weight of skeleton." They imply that *Galaxea* has a more massive and dense skeleton than *Tubastrea*. Superficially, this appears to be so. Comparisons of similar sized corallites (in diameter of the open or mouth end of the corallite and lengths), however, reveal that the skeletal mass of *Tubastrea* is about 70 to 80% that of *Galaxea* and that the skeletal densities are similar (*Tubastrea*, SD = 2.32 ± 0.61, n = 5; *Galaxea*, SD = 2.14 ± 0.24, n = 4).

Goreau *et al.* suggest that more appropriate measurements for the normalization of ^{45}Ca incorporation data are "tissue biomass protein, or nitrogen content." In fact, we gave normalized data using wet tissue mass and showed that, in these terms, the rate of ^{45}Ca incorporation in *Tubastrea* is approximately half that in *Galaxea*. I pointed out, however, that the mass ratio of tissue to skeleton in *Tubastrea* is almost 2.5 times that of *Galaxea*. This example illustrates the difficulty of using tissue mass protein, or nitrogen content for normalization when between-species comparisons are made. The underlying assumption is that these parameters are a measure of the surface area of the skeletogenic epithelium, that is, the calicoblastic (basal) ectoderm. This cell layer is highly attenuated, being only 1 to 3 μm thick in most cases, while the other three cell layers (aboral endoderm, oral endoderm, and oral ectoderm) vary in thickness up to approximately 50 μm, and the types of cells vary considerably between layers, between regions of a polyp, and particularly between species (*6*, *7*). Clausen and Roth (*3*) have suggested that "particularly in perforate corals, tissue content (and organic nitrogen) may be better correlated with volume than with surface area."

Even if the true surface area of the calicoblastic ectoderm could be measured, the information is not useful unless the sites of ^{45}Ca deposition during the incubation are known. Deposition in *Galaxea* occurs, in light, on the wall of the corallite, but not on the costae, and on the centrad regions of the septa. In this case, normalizing by the total surface area of the calicoblastic ectoderm (which covers the surface of the septa as well as the other parts of the corallite) would give inaccurate results. Preliminary results for *Tubastrea* indicate that short term (3 to 5 hours) of ^{45}Ca deposition may also not be uniform. (*8*).

In the light of the foregoing, it seems that calcification in terms of accretion (mass of new calcium deposited per total mass of calcium) as defined and used by Goreau (*5*) would be the most appropriate method for interspecific comparisons. A slightly modified version of this (mass of new calcium deposited per total mass of skeleton) is the method I used in my report.

I have suggested that my data on the mechanisms of calcification are not inconsistent with the model proposed by McConnaughey (*11*), who suggests that calcification may be viewed as a by-product of a CO_2-generating process for algal photosynthesis. Far from being a "misinterpretation of the acid-base reactions," this seems to be a well-considered proposal. The conversion of extracellular bicarbonate to CO_2 in the model may well involve carbonic anhydrase. In terms of this model, it makes sense that zooxanthellae may repress calcification in the dark when CO_2 is not required. Goreau *et al.* say that "cellular pH measurements by microelectrode" refute "the mechanism Marshall proposes." Actually, it is McConnaughey's proposal (*11*), and Kuhl *et al.* (*12*) do not state that their measurements are intracellular.

I agree that my measurements are not inconsistent with the existing literature because the only sufficiently detailed data are those on *T. micrantha* (9), which appear to support my proposal that azooxanthellate corals may calcify at rates similar to those of some zooxanthellate corals.

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22 March and 4 April 1996; accepted 26 July 1996

Imaging Substrate-Mediated Interactions

Surface defects, such as steps and adsorbed atoms and molecules, perturb the electronic structure of the surrounding surface. These perturbations greatly affect adsorbate structures, dynamics, and chemistry. We have now observed these perturbations directly with the use of scanning tunneling microscopy and have shown that they determine the structure and dynamics for benzene on Cu{111} that we had previously found (*1*). These substrate-mediated interactions have important implications for the atomic-scale mechanisms of film growth and heterogeneous selective catalysis.

There are three ways in which the electronic structure of a surface can be perturbed. First, the electron distributions at the steps are smoothed by a charge transfer from the top to the bottom of the step edge, the so-called Smoluchowski effect (*2*). Sec-

ond, electrons in surface states are scattered from surface features such as steps and adsorbates (3–6). Interference between the incident and reflected electron waves creates modulations in the surface local density of states (LDOS) surrounding the scatterer. These interferences thus augment and reduce the LDOS at specific surface sites for particular electron energies. The local holding potentials for adsorbed atoms and molecules thus vary with surface position. Both the Smoluchowski effect and these interferences have been previously shown for bare metal surfaces (3). Third, adsorption of atoms and molecules on surfaces also perturb the local surface electronic structure (7, 8). For benzene on Cu{111}, these perturbations extend several Cu lattice spacings from the molecules bound at step edges (8) (Fig. 1). It is this last perturbation that led to the adsorption sites in rows adjacent to the step edges as shown in our report (*1*).

The sites of addition of atoms and molecules are critical to the growth of films and nanostructures. Mobile species probe the surface to find favored adsorption sites. Substrate-mediated interactions can guide mobile adsorbates to particular sites of a growing structure. The ability of molecules to modify their local chemical environment indicates that with the appropriate choice of molecules and substrates we may be able to design self-assembling nanometer-scale and larger atomically precise structures. By substituting the proper moieties at the periphery of the constituent molecules, we could exercise control on and *define* the surrounding surface chemical environment and thus choose the alignment, proximity, and orientation of the appropriately substituted neighboring molecules (Fig. 2). Modification of the electronic structure of the surface by a feature such as a step edge or point defect can create nucleation sites for the structure. These molecules in turn generate adsorption sites for other molecules at the periphery of the structure by substrate-mediated interactions and by direct adsorbate-adsorbate interactions. Each subsequent step fits the previously defined electronic structure as in a jigsaw puzzle. By sequentially dosing the surface with various species, a great variety of different nanostructures may then be built.

Along similar lines, in selective heterogeneous catalysis, modulation of the surface LDOS surrounding an adsorbate spatially modulates both the reactivity and the reactant holding potential. Steric requirements may make certain configurations of colliding reactants more susceptible to reaction (9). Substrate-mediated interactions can align adsorbed reactants to put them in the correct orientation for reaction. By favorably orienting reactants and holding them together, the reactants may be guided to enter the reactive channel. In this case, the attempt frequency for reaction may approach the vibration frequency of the reactants rather than depending on a stochastic collision rate (*10*). Enhancement of the surface reaction rate may thus be optimized by careful selection of specific combinations of substrate, site, and reacting adsorbates. Feibelman and Hamann have proposed that at low coverage, catalytic poisoning is caused by long-range perturbation of the surface electronic structure at the Fermi level (*11*). Selective design of new high-yield catalysts may exploit substrate-mediated interactions. Specifically, the binding site for one reactant can be set up by a special surface site such as a step. Subsequent perturbation of the surface electronic structure by this adsorbate can then act to align another reactant favorably for reaction as in the pre-aligned van der Waals complexes used in photo-induced reactions in molecular beams (*12*) and on surfaces (*13*).

We are able to predict adsorbate binding sites and ordering based on known and measurable surface electronic properties. The extent to which the relative alignment and orientation of co-adsorbates can be controlled in this manner in order to facilitate reaction and self-assembly remains to be explored.

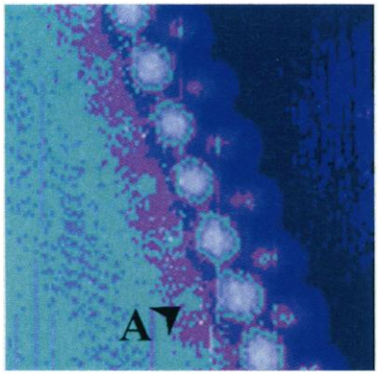

Fig. 1. Benzene molecules along a monatomic step edge on Cu{111} perturb the electronic structure of the adjacent surface thereby setting up adsorption sites for subsequent rows of molecules. An STM image of a 30 Å × 30 Å area of a Cu{111} surface recorded at 77 K is shown. The color scale highlights the modulation (A) of the empty surface electronic states above the step edge.

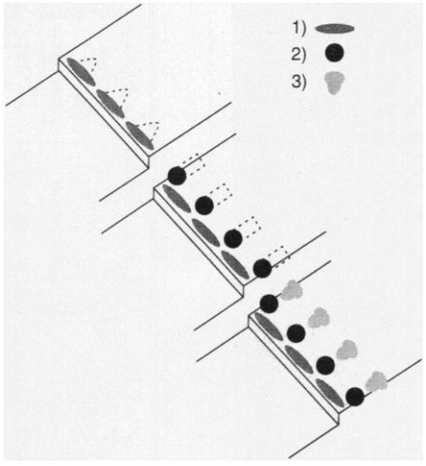

Fig. 2. Schematic of the application of substrate-mediated interactions to construct an atomically precise surface structure on the terrace above a monatomic height step edge. Perturbation of the surface electronic structure by the steps creates favorable adsorption sites for **1** at the step edges. Species **1** perturbs the surface electronic structure (indicated by dotted line), generating favorable adsorption sites for **2**. Adsorbate **2** in turn creates adsorption sites for **3**.

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11 May 1995; revised 27 September 1995; accepted 16 May 1996