

Our data argue in favor of the assembly of a "repressosome" complex that is dependent on both the configuration of Pit-1 on a specific cognate site and the actions of other DNA binding factors, which together dictate cell type-specific activation or repression of growth hormone gene expression. The allosteric effects of the high-affinity growth hormone promoter binding element on the configuration of Pit-1 appear to serve as one of the critical determinants (along with thyroid hormone receptor and a -161/-146 binding factor) of interaction with components of corepressor machinery in the appropriate cellular context (Fig. 5B). Allosteric effects of DNA binding sites have been suggested to mediate alternative activation or repression by other classes of transcription factors (32). Cofactor-dependent regulation is observed in the activities of Oct-1 on a TAATGARAT element where HCF and VP16 are recruited (33) and in the activities of Oct-1/Oct-2 on octamer elements where OCA-B/Bob1/OBF-1 is recruited, dependent on interactions with the POU_S and POU_H domains, as well as with specific nucleotides in the site (34-38). OCA-B/Bob1/OBF-1 is required for the activation of a subset of Oct-1/Oct-2-dependent genes in B cells, and it is tempting to speculate that, in its absence, a corepressor complex might, in some cases, be associated with Oct-1/Oct-2 on these sites.

In conclusion, we suggest that the selective patterns of hormone-encoding gene expression that define the three cell types of the Pit-1 lineage reflect, in part, differential association of distinct classes of cofactors, including N-CoR, with Pit-1, to mediate activation or repression. This strategy is likely to be prototypical of other cell type specification events in mammalian or-

ganogenesis and poses the challenge to now define other factors and/or signals that prevent recruitment of the repressor complex to the growth hormone promoter in somatotropes.

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11. The Prl-1P cocrystals belonged to space group P1 with unit cell dimensions of $a = 43.2 \text{ \AA}$, $b = 55.1 \text{ \AA}$, $c = 57.0 \text{ \AA}$, $\alpha = 89.5^\circ$, $\beta = 71.6^\circ$, and $\gamma = 78.0^\circ$. The GH-1 cocrystals belonged to space group C2 with unit cell dimensions of $a = 113.0 \text{ \AA}$, $b = 47.9 \text{ \AA}$, $c = 107.5 \text{ \AA}$, $\alpha = 90^\circ$, $\beta = 117.1^\circ$, and $\gamma = 90^\circ$. The structures of both complexes were solved by molecular replacement methods. The final R_{factor} for the Prl-1P complex is 0.239 (R_{free} of 0.312) for all data between 10 and 3.05 $\text{\AA}$, with root mean square deviations (rmsd's) on bond lengths and bond angles of 0.008 $\text{\AA}$ and 1.7°, respectively. The final R_{factor} for the GH-1 complex is 0.258 (R_{free} of 0.334) for all data between 10 and 3 $\text{\AA}$, with rmsd's on bond lengths and bond angles of 0.021 $\text{\AA}$ and 2.5°, respectively. For additional information, see supplementary Web material, available at www.sciencemag.org/feature/data/1055900.shl.
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39. We thank M. Frazer, H. Taylor, C. Arias, C. Lin, O. Hermanson, L. Staszewski, M. Magnuson, and A. F. Parlow for contributions and reagents; B. Smith and J. Feramisco at the University of California at San Diego Cancer Center Digital Imaging Shared Resource for deconvolution microscopy; D. Nadeau at the San Diego Supercomputer Center; the staff at Brookhaven National Laboratory and the Cornell High Energy Synchrotron Source for facilitating x-ray data collection; M. Fisher and P. Myer for help with the manuscript; and L. Shapiro, L. Erkman, O. Hermanson, J. Dasen, and V. Kumar for critical reading of the manuscript. This research was supported by grants to D.W.R. (NIH RO1 DK54802), M.G.R. (NIH RO1 DK18477), and A.K.A. (NIH RO1 GM49327).

19 September 2000; accepted 12 October 2000

REPORTS

Spin-Dependent Tunneling in Self-Assembled Cobalt-Nanocrystal Superlattices

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Self-assembled devices composed of periodic arrays of 10-nanometer-diameter cobalt nanocrystals display spin-dependent electron transport. Current-voltage characteristics are well described by single-electron tunneling in a uniform array. At temperatures below 20 kelvin, device magnetoresistance ratios are on the order of 10%, approaching the maximum predicted for ensembles of cobalt islands with randomly oriented preferred magnetic axes. Low-energy spin-flip scattering suppresses magnetoresistance with increasing temperature and bias-voltage.

exploit electron spin and the discreteness of electronic charge. For example, modern magnetic disc drives employ ultrasensitive read-heads based on the giant magnetoresistance (GMR) response of nanometer-thick metal multilayers (1). Also, two-dimensional (2D) arrays of spin-dependent tunnel junctions show promise for nonvolatile memory applications and will require reproducible tunnel barriers only 1 nm thick (2, 3). We have combined conventional lithography, chemical synthesis, and self-assembly to produce sub-100-nm, spin-dependent electronic devices with nanometer-scale control of material properties in all dimensions.

Self-assembly is an attractive nanofabrication technique because it provides the means to

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Increasing density requirements in the microelectronics and magnetic-storage industries continue to motivate the production of devices

that function reproducibly at ever smaller dimensions. Nanometer-scale control of material properties has already enabled technologies that

precisely engineer structures on the nanometer-scale over large sample areas. Self-organizing nanocrystal assemblies have already shown the degree of control necessary to address the challenges of building nanometer-scale technologies (4). Our experimental system combines the nanometer size-scale of granular thin films with the control and uniformity of lithographically patterned tunnel-junction arrays (junction area ~ 100 nm by 100 nm) (5, 6).

We produce monodisperse Co-nanocrystals (radius 5 nm, $\sigma = 5\%$) using high-temperature solution-phase synthesis. Details of the nanocrystal preparation have been previously described (7). We form Co-nanocrystals by injection of a strong reducing agent (lithium triethylborohydride) into a solution of anhydrous cobalt chloride in the presence of trioctylphosphine and oleic acid colloidal stabilizers (stirred at 200°C). The ratio of the metal salt and reducing agent to the stabilizer concentration controls nanocrystal size. The resulting crystal structure is ϵ -Co, a metastable cubic Co phase isomorphous with β -Mn. Each nanocrystal surface is coordinated by a monolayer of oleic acid, which provides a 2-nm-thick insulating organic coat. The nanocrystal superlattice is formed from a dispersion of the Co-nanocrystals in octane (7). Controlled evaporation of the solvent induces the nanocrystals to self-organize into an ordered array, with nanocrystal spacing (~ 4 nm) provided by the insulating organic capping group.

A high-resolution scanning electron microscope (SEM) image (Fig. 1A) shows that the shortest current-carrying path in this representative device contains only about seven

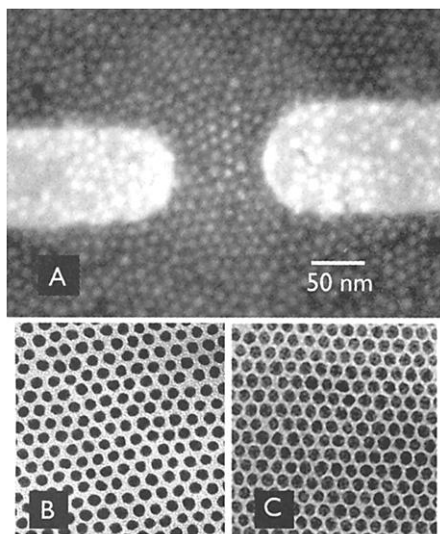


Fig. 1. (A) SEM image of self-assembled Co-nanocrystal superlattice device. (B) Transmission electron microscope image of a Co-nanocrystal superlattice before annealing, shows a ~ 4 -nm interparticle distance (nanocrystal diameter is 10 nm). (C) Co-nanocrystal superlattice after annealing (~ 2 -nm interparticle distance).

nanocrystals in series (8). The Co-nanocrystals form a hexagonal close-packed array, which is well ordered over the critical device dimension (~ 100 nm). The ~ 100 -nm-wide electrodes are defined using electron-beam lithography and lift-off of a 15-nm-thick AuPd metal film. As deposited superlattices are electrically insulating ($R > 1$ teraohm) because the organic capping groups provide a ~ 4 -nm interparticle spacing (Fig. 1B). Annealing the superlattice for 1 hour under reducing conditions (400°C, 95% Ar/5% H_2) converts the nanocrystal's internal structure to mixed hexagonal/face-centered cubic (7), and brings neighboring nanocrystals closer together (~ 2 nm, shown in Fig. 1C). The H_2 anneal also reduces the surface oxide layer which forms on nanocrystals during handling. In order to compensate for film shrinkage during the annealing, we typically deposit nanocrystal superlattices that are one to three monolayers thick. We report spin-dependent tunneling measurements of sub-100-nm test devices containing these periodic Co-nanocrystal arrays (9). Because of the device dimensions, only small numbers of nanocrystals are involved in electron transport.

The device current-voltage (I - V) characteristic (Fig. 2A) becomes increasingly nonlinear with decreasing temperature (T). At 300 K, the I - V curve is ohmic, with resistances on the order of 100 kilohm (corresponding 300 K superlattice resistivity $\rho \sim 10$ ohm-cm). The resistance increases monotonically with decreasing T , and for $T \lesssim 70$ K the I - V curve becomes nonlinear near-zero bias (see $T = 20$ K, 2 K in Fig. 2B). For $T < 12$ K, a finite voltage (V_T) is necessary to generate current through the nanocrystal array. In this device, we measure $V_T = 110$ mV at $T = 2$ K. All our devices show a distinct current threshold, although the specific value of V_T

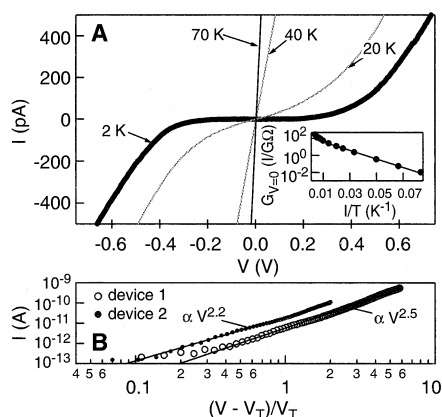


Fig. 2. (A) Device I - V characteristic, for $T = 2$ K (dark line) and 20, 40, and 70 K (light lines). (Inset) Plot of zero-bias conductance versus $1/T$. Data (circles) are well fit by theory (solid line) for $k_B T < U$. (B) For $V > V_T$, current displays a power-law dependence. The scaling exponents for the two devices shown are $\zeta = 2.2$ and 2.5.

varies from device to device due to offset-charge disorder in the array (10, 11). This I - V behavior is typical of the eight Co-nanocrystal devices we have measured, and has been observed for different nanocrystal arrays fabricated on the same substrate, on different substrates, and from different preparations of Co-nanocrystals. A complete Coulomb blockade of current ($R > 1$ teraohm) is evidence that nanocrystals in the array are electrically isolated. We calculate that current paths composed of ~ 16 -nm radius nanocrystals would result in an incomplete Coulomb blockade, even at the lowest experimental temperatures (2 K). This situation would only occur if the 5-nm radius nanocrystals had aggregated into physical contact during high-temperature processing.

Temperature dependence of the $V = 0$ conductance ($G_{V=0}$) provides strong evidence of the underlying nanocrystal uniformity. Low-voltage electron transport through an array of Coulomb islands is dominated by the energy to electrostatically charge individual nanocrystals. A simple model for an array of identical metal islands predicts a thermally activated behavior (12):

$$G_{V=0} \propto \exp\left[\frac{-U}{k_B T}\right] \quad (1)$$

where U is the activation energy to charge an electrically neutral nanocrystal and k_B is the Boltzmann constant. In this model, $U \equiv e^2/2C$, where C is the total capacitance of the particle to its surroundings and e is the charge of the electron. The Arrhenius form of Eq. 1 successfully describes $G_{V=0}$ for lithographically patterned tunnel-junction arrays (5, 6) because junction areas are precisely defined.

With a few exceptions (12, 13) the conductance of granular thin films does not follow simple thermal activation. By accounting for the varying particle sizes inherent to a granular film, one can show that $G_{V=0} \propto \exp[-\sqrt{U^*/k_B T}]$ (14), where U^* is an activation energy for the film. The characteristic $T^{-1/2}$ temperatures dependence of $G_{V=0}$ is a distinct signature of grain size nonuniformity. Model calculations for our experimental system indicate that $G_{V=0}$ deviates measurably from Eq. 1 when the nanocrystal size distribution (σ) exceeds 15% (5.0 nm ± 0.75).

A plot of $G_{V=0}$ versus $1/T$ (inset to Fig. 2A) shows that conduction in our Co-nanocrystal superlattices is well described by Eq. 1 for $k_B T < U$ (solid line). From the slope of the theoretical fit, we calculate $U = 10$ meV. In all our Co-nanocrystal devices, we measure $10 < U < 14$ meV. We estimate the interparticle capacitance $C = 1.0$ aF using

$$C \sim 2\pi\epsilon_0\epsilon r \ln\left(\frac{r+d}{d}\right) \quad (15),$$

where r is the nanocrystal radius (5 nm), $2d$ is the interparticle distance (2 nm), and ϵ is the dielectric

constant of the tunnel barriers (~ 2) (16). Each nanocrystal in the array has on average nine nearest neighbors (nn) (17), so $C_{nn} = 9.0$ aF, and $E_U \approx e^2/2C_{nn} \sim 9$ meV, in reasonable agreement with the value of U extracted from the data.

The voltage dependence of current (for $V > V_T$) depends on the number of accessible current paths through the superlattice. Theory predicts the current through a uniform array of islands to follow (11)

$$I \propto \left(\frac{V}{V_T} - 1 \right)^\zeta \quad (2)$$

(for $V > V_T$), where ζ is a scaling exponent that depends on array dimensionality. If only one preferred path (or a small number of paths) carries a majority of the current, then $\zeta \approx 1$ as the device is essentially one-dimensional. A 2D array (where all paths through a single-nanocrystal monolayer contribute) has a stronger voltage dependence. Analytical arguments predict $\zeta = 5/3$, although numerical simulations of finite-size 2D arrays give $\zeta \sim 2$ (11). Experimentally, 2D arrays of lithographically patterned tunnel junctions have shown $1.6 < \zeta < 2.1$ ($\Delta\zeta/\zeta \sim 12\%$) (5). Although there are no theoretical predictions for ζ in a 3D array, the scaling exponent no doubt increases for greater numbers of current-carrying paths. Measurements of granular thin-film materials have shown current scaling above V_T , with ζ ranging from ~ 2 to 3.5 , depending on film thickness (18).

In our nanocrystal devices we measure $2.2 < \zeta < 2.7$ ($\Delta\zeta/\zeta \sim 9\%$), implying an array dimensionality slightly higher than 2D and consistent with our experimental geometry. Thus, the scaling exponent confirms that all paths through the superlattice can contribute to device conductance. A plot of I versus $(V/V_T - 1)$ (Fig. 2B) shows that for $V > V_T$, the current follows a power-law dependence for over three orders of magnitude. The variation in ζ from device to device ($\sim 9\%$) is comparable to that measured for lithographically patterned arrays (junction areas ~ 100 nm by 100 nm).

Magnetization (m) versus applied field (H) measurements of a Co-nanocrystal superlattice (Fig. 3A) show a clear magnetic hysteresis at $T = 5$ K, meaning that the Co-nanocrystals are ferromagnetic. The coercive field (H_c) for the assembly is ~ 0.05 T. The magnetic hysteresis vanishes at a blocking temperature $T_b \approx 80$ K.

The direct current (dc) magnetoresistance changes by $\Delta R/R_{\max} \approx 8\%$ (at $T = 2$ K) between $H = 0$ and 0.4 T (Fig. 3B). In all our devices, we find magnetoresistance ratios between 5 and 12%. We bias the device with a dc voltage (0.4 V for the data in Fig. 3B) to overcome the Coulomb blockade of current, and we apply H in the plane of the Co-nanocrystal superlattice. The device resis-

tance increases as H is lowered from saturation through ~ 0.1 T and nanocrystal magnetic moments begin to randomize. After H passes through zero, the resistance reaches a maximum near H_c , when nanocrystal moments are maximally antialigned. For fields beyond H_c , the resistance again decreases to the initial value. The magnetoresistance is hysteretic at this temperature, and reflects the nanocrystal ferromagnetism. Some fine structure in the magnetoresistance is reproducible (small peaks near ± 0.075 T repeat in both directions and are noted on the graph in Fig. 3B). Because current paths contain only ~ 10 nanocrystals, the conductivity is sensitive to realignment of single nanocrystal moments. Detailed studies of fine structure in the magnetoresistance will provide information about the magnetization reversal process in the nanocrystal superlattice.

We quantitatively understand the magnitude of the device magnetoresistance (5 to 12%) by noting that the tunneling rate, Γ , between two nanocrystals with magnetic moments is (19)

$$\Gamma = G_0(1 + P^2 \cos \theta) \quad (3)$$

where P is the conduction-electron polarization of the material, θ is the relative angle between the two moments, and G_0 is the spin-independent tunneling rate. For nanocrystal moments oriented along the same axis, $\theta = 0$ and π for parallel and antiparallel orientations, respectively. The difference in resistance between parallel ($\theta = 0$) and antiparallel ($\theta = \pi$) configurations is

$$\begin{aligned} \frac{\Delta R}{R_{\max}} &= \frac{(R_{\theta=\pi} - R_{\theta=0})}{R_{\theta=\pi}} = \frac{(\Gamma_{\theta=0} - \Gamma_{\theta=\pi})}{\Gamma_{\theta=0}} \\ &= \frac{2P^2}{1 + P^2} \end{aligned} \quad (4)$$

For nanocrystal magnetic moments with no preferred orientation, the relative angle between moments takes a random value between 0 and π . The maximum $\Delta R/R_{\max}$ is then given by $\Delta R/R_{\max} = P^2/(1 + P^2)$ (19), which is 50% of the fully oriented value (Eq. 4). Using the bulk

value for the conduction electron polarization in Co [$P = 0.34$ (20)], we calculate $\Delta R/R_{\max} = 10.3\%$ for our experiment, which agrees well with the measured values. This $\Delta R/R_{\max}$ sets a lower bound for the achievable magnetoresistance ratio in a nanocrystal superlattice device. Nanocrystal superlattices in which magnetic moments are preferentially aligned would have magnetoresistance ratios, which approach the fully oriented value given by Eq. 4.

There have been several reports of enhancements to $\Delta R/R_{\max}$ for granular thin films at low temperature (13, 21–24). The proposed mechanism for this enhancement involves higher order co-tunneling processes, which transfer electrons across several junctions simultaneously (25). Because our devices show a complete Coulomb blockade and a distinct V_T for current turn-on (below which only co-tunneling is possible), we can experimentally verify that current contributions from co-tunneling are extremely small (< 100 fA). Co-tunneling rates (Γ_Q) are sharply suppressed by increasing numbers of junctions (n) in the array [$\Gamma_Q \sim (G_0)^{-n}$], so that in our devices ($n \sim 10$) the likelihood of an electron traversing the array solely via cotunneling is exceedingly small. The lack of appreciable co-tunneling is consistent with measured $\Delta R/R_{\max}$ values, whose magnitudes are explained in terms of sequential tunneling (Eq. 4).

With increasing temperature above 2 K, $\Delta R/R_{\max}$ decreases rapidly (Fig. 4). When the temperature reaches 20 K, $\Delta R/R_{\max}$ is less than 10% of its maximum value. We expect minimal reduction in the Co-nanocrystal magnetic moments at this temperature because magnetization measurements of similar Co-nanocrystal assemblies indicate a blocking temperature of ~ 80 K. Our data are consistent with a thermally activated spin-flip scattering mechanism which follows (solid line in Fig. 4) (21, 26, 27)

$$\frac{\Delta R}{R_{\max}} \propto 1 - \exp\left[\frac{-E_{mr}}{k_B T}\right] \quad (5)$$

In Eq. 5, E_{mr} (≈ 0.33 meV ≈ 4 K) is the characteristic energy associated with the spin-flip scattering process. At present we cannot

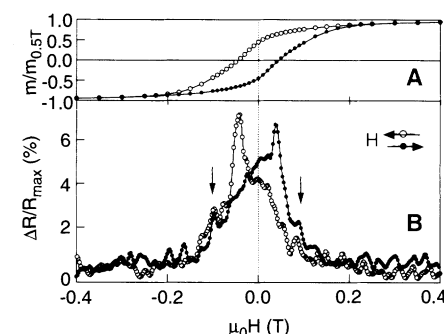


Fig. 3. (A) Magnetization of a Co-nanocrystal film at 5 K. (B) Magnetoresistance of Co-nanocrystal device at 2 K. Arrows indicate reproducible fine structure.

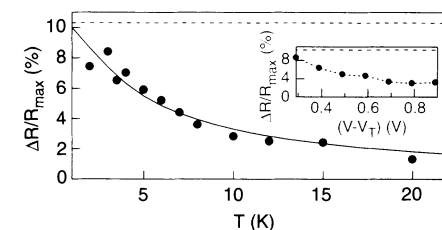


Fig. 4. Temperature dependence of magnetoresistance and fit to Eq. 5 (solid line). Dashed line indicates the maximum expected value of $\Delta R/R_{\max}$ for randomly oriented moments. (Inset) Voltage dependence magnetoresistance (dotted line serves as a guide).

specify the exact origin of this low-energy scattering process, although we speculate that it is caused by antiferromagnetic cobalt-rich oxide (Co_3O_4) on nanocrystal surfaces.

Because current through the nanocrystal array is carried by parallel conduction paths containing differing numbers of nanocrystals, the device magnetoresistance ratio is less sensitive to applied voltage. A plot of $\Delta R/R_{\text{max}}$ versus $(V - V_T)$ (Fig. 4, inset) shows that for $(V - V_T) = 900$ mV, $\Delta R/R_{\text{max}}$ is reduced to $\sim 35\%$ of its maximum. Estimating $n \sim 10$ nanocrystals in the shortest conduction path, this bias voltage implies an excess $(V - V_T)/n = 90$ mV across each junction. The corresponding effective temperature, $e(90 \text{ meV})/k_B \sim 1000$ K, suppresses $\Delta R/R_{\text{max}}$ along this particular path. Parallel current paths through the array containing differing numbers of nanocrystals each have distinct voltage thresholds (V_{Tpath}) for turn-on. Increasing bias voltage opens new current-carrying paths, so that whereas $\Delta R/R_{\text{max}}$ is suppressed for those channels where $V > V_{\text{Tpath}}$, the paths in which V is approximately equal to V_{Tpath} will continue to show strong magnetoresistance. This argument explains the experimental observation that bias voltage and temperature have a similar effect on $\Delta R/R_{\text{max}}$ in single magnetic-tunnel junctions (28), whereas measurements of granular magnetic thin films show $\Delta R/R_{\text{max}}$ is less sensitive to voltage (relative to temperature) (13).

Self-assembled Co-nanocrystal superlattices are model experimental systems for studying magnetotransport in nanostructured materials. The reported electrical measurements demonstrate spin-dependent tunneling in nanoscale devices formed of highly uniform magnetic-nanocrystal arrays.

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- We thank C. Kagan for helpful discussions and for critical readings of this manuscript.

10 July 2000; accepted 29 September 2000

The Role of Mg^{2+} as an Impurity in Calcite Growth

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Magnesium is a key determinant in CaCO_3 mineralization; however, macroscopic observations have failed to provide a clear physical understanding of how magnesium modifies carbonate growth. Atomic force microscopy was used to resolve the mechanism of calcite inhibition by magnesium through molecular-scale determination of the thermodynamic and kinetic controls of magnesium on calcite formation. Comparison of directly measured step velocities to standard impurity models demonstrated that enhanced mineral solubility through magnesium incorporation inhibited calcite growth. Terrace width measurements on calcite growth spirals were consistent with a decrease in effective supersaturation due to magnesium incorporation. $\text{Ca}_{1-x}\text{Mg}_x\text{CO}_3$ solubilities determined from microscopic observations of step dynamics can thus be linked to macroscopic measurements.

Magnesium is an important modifier of CaCO_3 morphology and growth in natural waters (1–3). Accordingly, changes in the seawater Mg/Ca ratio may have governed the polymorphic transitions observed in carbonate biominerals during the geologic past (4, 5). Although the presence of Mg^{2+} in calcium carbonate biominerals is increasingly being used as an empirical paleothermometer (6–10), the physical basis by which Mg^{2+} modifies carbonate growth has yet to be discerned. Bulk studies have suggested that calcite growth is inhibited through either step-blocking by Mg^{2+} adsorption and slow dehydration (11–14) or enhanced mineral solubility associated with Mg^{2+} incorporation (15). Here we address this controversy over the molecular-scale mechanism by which Mg^{2+} inhibits calcite growth, by comparing in situ experimental measurements to theoretical crystal growth impurity models.

We used fluid-cell atomic force microscopy (AFM) to make in situ observations of

calcite crystallization onto a seed crystal in a flow-through environment (16). Single-sourced growth spirals emanating from screw dislocations on the calcite surface were imaged in Contact Mode (Digital Instruments, Santa Barbara) under controlled solution conditions at 25°C . Supersaturated growth solutions were prepared from CaCl_2 and NaHCO_3 . Mg^{2+} was introduced to the growth solutions as MgCl_2 , and inductively coupled plasma-atomic emission spectroscopy was used to confirm the purity of all reactants. The pH of each growth solution was adjusted to 8.50 by small additions of NaOH (17). The ionic strength of each solution was fixed between 0.115 and 0.119 M, and the ratio of calcium-to-carbonate activity was held from 0.99 to 1.01. The chemical speciation of each solution was modeled by means of a numerical code that implemented the Davies equation for activity determinations (18). Monomolecular step velocities (v_s) and terrace widths (λ) were directly measured on growth spirals as a function of both supersaturation (σ) and Mg^{2+} activity. The rate of solution input was adjusted to yield step velocities that were independent of flow rate, thereby ensuring that growth was not limited by mass transport to the surface. Step velocity was determined as displacement from a fixed reference point (i.e., the dislocation source)

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