FINAL REPORT

PROJECT TITLE: Quantifying Silica Reactivity in Subsurface Environments: An Integrated Experimental Study of Quartz and Amorphous Silica to Establish a Baseline for Glass Durability

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PROJECT OBJECTIVE AND BACKGROUND:

An immediate EM science need is a reliable kinetic model that predicts long-term waste glass performance. A framework for which the kinetics of mineral-solution reactions can be used to interpret complex silicate glass properties is required to accurately describe the current and future behavior of glasses as synthetic monoliths or natural analogs. Reaction rates and mechanisms are essential elements in deciphering mineral/material reactivity trends within a compositional series or across a matrix of complex solution compositions. An essential place to start, and the goal of this research,

is to quantify the reactivity of crystalline and amorphous SiO₂ phases in the complex fluids of natural systems.

Perhaps the most important motivation for quantifying SiO₂ reactivity in subsurface environments is that an understanding of fundamental controls on the reactivity of simple Si—O bonded phases establishes baseline behavior for silica phases widely found in waste storage environments. Host rock silicate minerals dominate virtually every repository rock-water system. Further, complex silicate glasses will be the frontline of defense in containing radioactive wastes in both interim and long-term storage strategies. However, we have little quantitative understanding of pure SiO₂ reactivity in the solutes of natural and perturbed groundwaters even though current EM strategy calls for dispersal of waste into silica-based glass materials. Findings will establish quantitative relationships between silica reactivity and complex solution chemistries never investigated which are presently speculative at best. Further, we will be able to uncover underlying principles that govern how solutes affect silica reactivity in a systematic and predictable way.

FINAL REPORT OF FINDINGS:

The new research project was initiated on February 1, 2001 and has now been completed. We focused the funding on the costly experimental work rather than extensive travel. In the end, our efforts paid off with findings in all aspects of the research activities that have been described by others as “transformational”.

A particularly exciting outcome is the paper recently published in Dove et al. (2005, PNAS). Thanks to the investment made by this EMSP project we worked for three years on the question of how driving force to the corrosion reaction mediates the kinetics of silica dissolution. The findings exceeded our highest expectations by making a fundamental new discovery *that would not have been possible without this EMSP project*. Though the new insights challenge the status quo held by the traditional community, some have already acclaimed this work as the most important new insight in mineral dissolution for more than 50 years.

We show that seemingly disparate data sets and dissolution regimes can be unified within a single model by analyzing mineral dissolution using the same physical

picture used for crystal growth. In fact, our work found that the entire spectrum of growth and dissolution can be viewed within a single continuum, in which transitions from one dominant mechanism to another are determined by a single, simple consideration, namely which one produces the greatest step density. This tour de force was recently highlighted by both *Science* and *Elements*, in their Editor's Choice articles for its significance.

Owing to the breakthrough in the PNAS paper, we realized a new mechanism-based way of understanding glasses. This was part of our original goal for the EMSP project and has taken some time, but is still forthcoming. Again, thanks to the support of this project, we are about to make a new breakthrough in understanding glass dissolution in an unprecedented new way. We foresee that this forthcoming publication will be as significant as our 2005 *PNAS* article.

A. Interactions with Users - Tank Focus Area:

The P.I., Dove, interacted with TFA scientists and engineers on the problems of waste glass properties. Results of our EMSP-funded research interfaced well with the efforts of Dove's former EMSP-funded postdoc, Dr. Jonathan Icenhower, and his group at PNNL. Another of the EMSP postdocs is now a Research Scientist at Lawrence Berkeley Laboratory. Both were sought after for their expertise gained in our lab. This facilitated information transfer from the 'university lab to user' environments. Similarly, former EMSP-funded graduate student, Troy Lorier, now works with the Glass Chemistry group (Dr. Bill Holtzscheiter) at Westinghouse Savannah River.

B. Publications:

Lorier, T. (2000) The dissolution kinetics of quartz and amorphous silica in natural waters:

A baseline for silica reactivity. Georgia Institute of Technology, *M.S. Thesis*.

Craven, C.M. (2000) The effects of electrolyte solution composition on the surface charge development of silica. Georgia Institute of Technology, *M.S. Thesis*.

Karlsson, M., C.M. Craven, **P.M. Dove** and W.H Casey (2001) Surface charge concentrations on silica in different 1.0 M metal chloride background electrolytes and implications for dissolution rates. *Aquatic Geochemistry*, 7, p. 13-32.

Dove, P.M. and K.J. Davis (2004) "Inorganic controls on mineral formation" In *From Fluid-Solid Interfaces to Nanostructural Engineering*", eds. J.J. De Yoreo and X.Y. Liu, Plenum/Kluwer Academic Press.

Dove, P.M. and C.M. Craven (2005) Silica surface charge in alkali chloride solutions reveals roots of ionic specificity. *Geochimica Cosmochimica Acta*. v. 69, 4963-4970.

Dove, P.M., N. Han and J.J. De Yoreo (2005) Classical nucleation theory predicts the dissolution and growth kinetics of quartz and silicate minerals. *Proceedings of the National Academy of Sciences*. v. 102, p. 15357-15362.

He, T.Y. and **P.M. Dove** (in review) The effect of divalent cations on the dissolution kinetics of amorphous silica at 60°C: Investigating the origins of cation-specific rate enhancement. *Geochimica Cosmochimica Acta*.

He, T.Y. and **P.M. Dove** (in preparation) The effect of divalent cations on the dissolution kinetics of quartz and the control of driving force at 200°C. *Geochimica Cosmochimica Acta*.

Dove, P.M. and T. Lorier (in preparation) Calcium and magnesium levels control enhanced dissolution of silica. For *Geology*.

C. Recent Conference Abstracts:

Dove, P.M., N. Han and J.J. De Yoreo (2005) Classical Nucleation Theory Explains Mineral Growth and Dissolution Within a Mechanistic and Quantitative Framework. *AGU Fall Meeting*, San Francisco. *Geothermal/Tectonophysics Special Session*.

Dove, P.M., N. Han and J.J. De Yoreo (2005) Classical nucleation theory predicts the dissolution and growth kinetics of quartz and silicate minerals. **Keynote Lecture**, Mineral Surface Reactivity, V.M. Goldschmidt Conference, Moscow, Idaho.

Craven, C. and **P.M. Dove** (2003) Control of solvation entropy on the electrostatic adsorption of cations onto silica. *Geological Society of America Conference*, Seattle, Washington.

He, Y. Thomas and **P.M. Dove** (2004) Divalent metals enhance silica dissolution kinetics by a predictable relation. *American Chemical Society*, Anaheim, California.

D. Awards, Invited Activities, and Advancement of Geochemistry:

2005 **DOE Best University Research Award:**

Analytical and Isotope Geochemistry Symposium

2004 **Board of Directors**, Geochemical Society

2003 **Best Poster Award:** American Conference on Crystal Growth.

2003 **Organized Special Session:** *Biomineralization*, *Geological Society of America Annual Meeting*, Seattle

2003 **Organized Special Sessions:** *Biomineralization Processes and Mechanisms* and *Impacts of Biomineralization on Earth Environments*, at *American Geophysical Union Meeting*, San Francisco.

2003 **Co-editor:** *Reviews in Mineralogy and Geochemistry Volume 54:*

Biomineralization with Short-course Workshop with J.J. DeYoreo and S. Weiner.

2002 **Invited Speaker:** Marcus Wallenberg Foundation for International Scientific Cooperation: Biogeochemistry, *Swedish Royal Academy of Science*, Stockholm

2002 **Paul Gast Lecturer:** V.M. Goldschmidt Conference, Davos, Switzerland (P.M. Dove)

2002 **Invited Speaker:** Fall AGU special session *Nanoparticles in the Environment*, San Francisco

2001 **Outstanding Student Paper Award**, Hydrology Section, American Geophysical Union (Mr. Colin Craven)

2000 **Fellow**, Mineralogical Society of America

(P.M. Dove)

1999 **DOE Best University Research Award**, Interfacial Processes Symposium

(P.M. Dove)

PROJECT FINDINGS:

Craven and Dove (2005, GCA). The surface charge density of colloidal SiO₂ (Aerosil 380) was measured in alkali chloride (0.067 and 0.20 M LiCl, NaCl and KCl) and alkaline earth chloride (0.067 M MgCl₂, CaCl₂, SrCl₂, BaCl₂) solutions. Measurements were conducted at 25°C by potentiometric titrations using the constant ionic medium method in a CO₂-free system. The experimental design measured surface charge for solutions with constant ionic strength as well as constant cation concentration. Alkali chloride solutions promote negative surface charge density in the order LiCl < NaCl < KCl to give the ‘regular’ lyotropic behavior previously reported. In contrast, the alkaline earth chloride solutions exhibit a reversed lyotropic trend with increasing crystallographic radius where increasing negative charge is promoted in the order BaCl₂ < SrCl₂ < CaCl₂ < MgCl₂.

Figure. 1

The origin of the opposing affinity trends is probed by testing the hypothesis that this reversal is rooted in the differing solvent structuring characteristics of the IA and IIA cations at the silica-water interface. This idea arises from earlier postulations that solvent structuring effects increase entropy through solvent disordering and these gains must be much greater than the small, positive enthalpy associated with electrostatic interactions. By correlating measured charge density with a proxy for the solvent-structuring ability of cations, this study shows that silica surface charge density is maximized by those electrolytes that have the strongest effects on solvent structuring (Fig. 1). We suggest

that for a given solid material, solvation entropy has a role in determining the ionic specificity of electrostatic interactions and reiterate the idea that the concept of lyotropy is rooted in the solvent-structuring ability of cations at the interface.

He and Dove (in review. A, in prep. B, GCA) Reliable kinetic models that predict long-term waste glass performance require accurate baseline knowledge of how major solutes and metals affect silica reactivity. The effects of 2+ cations as alkaline earth (Mg, Ca, Sr, Ba) and transition metal (Mn, Co, Cu, Ni, Zn, Cd) elements on the dissolution of amorphous silica, SiO₂(am), were determined at 60°C in semi-batch reactors at near-

neutral pH (pH 5.7). Experimental measurements show that all cations increase SiO₂(am) dissolution rates by 10-50 times compared to measurements in DI H₂O. The maximum degree of rate enhancement does not correlate with d electron configuration of the metals, but does follow a simple trend that correlates with Z^2/r (where r = hydrated radius) and the electronegativity of the corresponding cations as $EN_{Si} - EN_{Me}$ (**Figure 2**). All cations except nickel follow this relation. Our findings reiterate the possible role of cation solvation properties in mediating the kinetics of Si-O bond hydrolysis.

Figure 2

Dove and Lorier (in preparation, Geology) The global cycling of silicon is closely linked to factors that control the dissolution of mineralized silica. Here we establish controls of major cations in terrestrial waters (Na^+ , K^+ , Ca^{2+} , Mg^{2+}) on dissolution kinetics when they act in concert and show that enhanced rates are governed by calcium and magnesium concentrations. Low levels of calcium and magnesium cause large differential increases in rate even when sodium or potassium levels are 100X greater as shown in **Figure 3**.

Figure 3. Dissolution rates ($\text{mol m}^{-2} \text{s}^{-1}$) of quartz and amorphous silica at 200°C are shown as isotachs on a ternary diagram that represents compositions of solution mixtures containing the major solutes. The total metal concentration across the ternary space is equal to $3.18 \times 10^{-3} \text{ m}$ while ionic strength varies from $10^{-2.49}$ to $10^{-1.72}$. Color contours show that the variations in dissolution rate with changing proportions of calcium, magnesium and sodium (sodium = potassium) are primarily controlled by the relative concentrations of calcium and magnesium. Sodium controls rate only when present at concentrations that are $>200\times$ greater than calcium and magnesium (yellow indicates compositional regions where sodium has a 50% contribution to the rate enhancement). Dissolution rates in any of these solute mixtures are faster than 'pure water' by a factor of 17-85 and 13-40 for quartz and amorphous silica, respectively.

Our findings demonstrate that calcium and magnesium levels have dominant roles in enhancing the dissolution of SiO_2 and likely regulate rates of silica release into natural waters.

Dove et al. (2005, *PNAS*) The central control of mineral weathering on biogeochemical systems has motivated studies of dissolution for over 50 years. A complete physical picture that explains widely observed variations in dissolution behavior is lacking and some data show apparent serious, inconsistencies that cannot be explained by the largely-empirical kinetic ‘laws’. In this paper, we show that mineral *dissolution* can, in fact, be understood through the same mechanistic theory of nucleation developed for mineral *growth*. In principle, this theory should describe dissolution but has never been tested. By generalizing nucleation rate equations to include dissolution, we arrive at a model that predicts how quartz dissolution processes change with undersaturation from step retreat, to defect-driven and homogeneous etch pit formation. This reveals that the ‘salt effect’, recognized almost 100 years ago, arises from a crossover in dominant nucleation mechanism to greatly increase step density. The theory also predicts the dissolution kinetics of major

weathering aluminosilicates— kaolinite and K-feldspar. In doing so, it resolves controversial discrepancies in reported kaolinite data by invoking a temperature-activated transition in the nucleation process. Though dissolution by nucleation processes was previously unknown for oxides or silicates, our mechanism-based findings are consistent with recent observations of demineralization in biological minerals. Nucleation theory may be the missing link to unifying mineral growth and dissolution into a mechanistic and quantitative framework across the continuum of driving force.

Appended to this document:

[*PNAS* article](#)

[*Editors Choice \(Science\)*](#)

[*Editor's Pick \(Elements\)*](#)

BUDGET DATA: Spending for the project is complete. The original budget was appropriate.

FINAL: We have completed the stated objectives of the project. The final product of this sponsored research exceeded the original work plan with strong and important, fundamental findings. The scientific community (and I) thank you for the opportunity to make these contributions to new knowledge. P.M. Dove

INFORMATION ACCESS: Please contact dove@vt.edu with any questions or to request reprints/preprints of our findings.

Mechanisms of classical crystal growth theory explain quartz and silicate dissolution behavior

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The central control of mineral weathering rates on biogeochemical systems has motivated studies of dissolution for more than 50 years. A complete physical picture that explains widely observed variations in dissolution behavior is lacking, and some data show apparent serious inconsistencies that cannot be explained by the largely empirical kinetic “laws.” Here, we show that mineral dissolution can, in fact, be understood through the same mechanistic theory of nucleation developed for mineral growth. In principle, this theory should describe dissolution but has never been tested. By generalizing nucleation rate equations to include dissolution, we arrive at a model that predicts how quartz dissolution processes change with undersaturation from step retreat, to defect-driven and homogeneous etch pit formation. This finding reveals that the “salt effect,” recognized almost 100 years ago, arises from a crossover in dominant nucleation mechanism to greatly increase step density. The theory also explains the dissolution kinetics of major weathering aluminosilicates, kaolinite and K-feldspar. In doing so, it provides a sensible origin of discrepancies reported for the dependence of kaolinite dissolution and growth rates on saturation state by invoking a temperature-activated transition in the nucleation process. Although dissolution by nucleation processes was previously unknown for oxides or silicates, our mechanism-based findings are consistent with recent observations of dissolution (i.e., demineralization) in biological minerals. Nucleation theory may be the missing link to unifying mineral growth and dissolution into a mechanistic and quantitative framework across the continuum of driving force.

silica | kinetics | mineralization

Over long time scales, the geochemistry of earth systems is, in large part, controlled by the kinetics of silicate mineral dissolution. Because waters contain a wide variety of solute types and concentrations, including significant levels of aqueous silica, there is considerable need to understand the dependence of silicate mineral dissolution rates on chemical driving force, as measured by the extent of undersaturation. This need has motivated intense investigations of both mineral weathering and the corrosion behavior of silica-based glasses.

Basic thermodynamic principles predict that mineral dissolution rates should increase with increasing driving force or chemical potential; however, experimental studies of major silicate minerals show that this dependence is complex. A further complication is the so-called “salt effect” reported for quartz, SiO₂, whereby the dissolution rate of this oxide end-member to all silicates is increased up to 100 times in the presence of the major cationic solutes found in natural waters (Na⁺, K⁺, Ca²⁺, Mg²⁺) (1–3). In contrast, dissolution rates of silicate minerals have only a weak sensitivity to the introduction of electrolytes (4). To explain these behaviors, many of the widely used rate models are based on variants of transition state theory and assume microscopic reversibility (5–7). Their shortcomings raise the question of whether or not the mechanistic models developed in the last few decades to so successfully explain crystallization can be used to resolve the confusion surrounding mineral dissolution.

Scheme 1.

Twenty years ago, a mechanistic model of nucleation-driven crystal growth was introduced that described growth kinetics in terms of four primary parameters: temperature T , supersaturation σ , step edge energy α , and step kinetic coefficient β (8, 9). By examining energy barriers to growth, the theory considered the probability of growth at dislocation defects vs. growth by nucleation of two-dimensional (2D) adatom islands either at impurity defects or homogeneously across the surface, as illustrated in Scheme 1.

This same theory also should apply to dissolution by analogous processes that also assume rates are controlled through T , σ , α , and β , but this hypothesis has never been tested. Application of this formalism to dissolution assumes that, in analogy to growth, it may occur by activating “corrosion” either at dislocation defects or by nucleation of 2D vacancy islands at impurities or homogeneous sites, as illustrated in Scheme 2.

Indeed, by using this approach, we can quantitatively explain the dissolution kinetics of quartz and of the major silicate weathering minerals, feldspar (KAlSi₃O₈) and kaolinite [Al₂(Si₂O₅(OH)₄]. We also show that the principle of detailed balancing (5) is only applicable to quartz dissolution at very near to equilibrium conditions where corrosion occurs by simple step edge retreat.

Methods

Dissolution Experiments. Dissolution-rate experiments used the 300- to 425- μ m fraction of pure quartz sand (Destin, FL). The material was pretreated with 30% H₂O₂ for 24 h, then alternately washed with 10% HNO₃ and distilled deionized water. Specific surface area of the final material was determined in triplicate (Micromeritics, Norcross, GA). Mixed flow-through reactors constructed of commercially pure titanium were used to measure the rate of silica production at 200°C for the overall reaction

Scheme 2.

Abbreviation: AFM, atomic force microscopy.

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Table 1. Treatment conditions for (100) quartz surfaces

Number	Solution	Ω	σ
①	No electrolyte	0.10	-2.3
②	0.0167 M CaCl_2	0.10	-2.3
③	0.0167 M CaCl_2	0.65	-0.4
④	0.0167 M CaCl_2	0.90	-0.1

at steady-state conditions using established methods (3). The solutions were prepared to specific values of undersaturation by adding carefully characterized levels of the monomeric silicic acid, H_4SiO_4 . Some silica solutions also contained reagent-grade salts (Aldrich) using 0.05 M NaCl or 0.0167 M $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$ such that total ionic strength was constant at 0.05 M. All input solutions had circumneutral pH and calculated *in situ* pH (pH_T) of ≈ 5.7 . The degree of undersaturation, σ , is defined by

$$\sigma = \ln \Omega = \ln(C/C_e), \quad [2]$$

where C and C_e are the measured and equilibrium concentrations of H_4SiO_4^0 . We use concentrations instead of activities because H_2O and H_4SiO_4^0 have activity coefficients very near unity for the conditions of our experiments. A value of $C_e = 10^{-2.4}$ M SiO_2 (236 ppm SiO_2), obtained from our dissolution experiments, is used to calculate undersaturation, σ .

Atomic Force Microscopy (AFM) Imaging. In parallel experiments, natural (100) prismatic surfaces of euhedral quartz crystals (Herkimer, NY) were exposed to the solution conditions provided in Table 1. The rationale for these choices will become clear later.

The surfaces were prepared as thin slices taken from the natural crystal surface and restrained in a hydrothermal mixed flow-through reactor using titanium screen. Durations of each treatment were determined by using measured dissolution rates to calculate the amount of reaction time necessary to give equal silica production ($0.010 \text{ mol}\cdot\text{m}^{-2}$) for each treatment. Thus, etching times ranged from 28 days to 4 h. Resulting surface morphologies were examined by AFM under a drop of water at ambient conditions.

Results

Kinetic measurements of quartz dissolution show a complex dependence on saturation state (Fig. 1a). At the low driving force of near-equilibrium conditions, dissolution rates are inversely correlated with Ω and the rate-enhancing effect of electrolytes is small (1–4 $\times$, Fig. 1b). This result indicates that salts have relatively little effect on quartz dissolution at the near-equilibrium conditions commonly found in geothermal systems with large rock/water ratios or long contact times. When the driving force to reaction is higher ($\Omega < 0.70$) rates acquire a nonlinear dependence on undersaturation. In the absence of electrolytes, quartz exhibits the characteristic “dissolution plateau” also reported for gibbsite and kaolinite (6, 10) (Fig. 1a). In contrast, rates measured in solutions that also contain 0.05 M NaCl or 0.0167 M CaCl₂ become up to 100 times faster with decreasing Ω . This salt-promoted rate enhancement at low Ω , the so-called salt effect, is unique to quartz (3), and Fig. 1a *Inset* shows that this effect is highly dependent on Ω .

Discussion

A mechanism-based explanation for the kinetic behavior in Fig. 1a is found in the dislocation and 2D nucleation theories developed for crystal growth (8, 9, 11). A brief description of our application to dissolution is as follows. The rate at which a crystal dissolves is controlled by the density of steps on the surface. These steps can be preexisting on the initial crystal surface or at the crystal edges, emerge from dislocation sources, or be created by nucleating new vacancy islands. Whichever source creates the greatest step density will dominate the dissolution process. Vacancy islands are initiated

Fig. 1. Measured rates of quartz dissolution vs. saturation state (Ω) show the dependence on driving force and the presence or absence of simple electrolyte salts. Calculated experimental errors indicate 1SD of the mean estimate and are illustrated for values larger than the symbol diameter. (a) Logarithm of rate vs. saturation state in water (blue circles), 0.0167 M CaCl_2 (red diamonds), and 0.05 M NaCl (green triangles). Numbers correspond to conditions that produced the surface structures in Fig. 2, and gray zones show undersaturation range where transitions occur in the dominant dissolution mechanism. *Inset* uses a linear ordinate to better illustrate the exponential dependence of rate on driving force when salts are introduced. (b) Expanded view of rate dependence on Ω shows the linear dependence on saturation at near-equilibrium conditions. This region is where the widely accepted first-order rate dependence such as Eq. 8 applies. Eq. 8 is fit to the data by forcing rate to zero at $\Omega = 1.0$ as denoted by open symbols.

by removal of molecules from the otherwise perfect crystal surface. These pits will, on average, grow provided they exceed a critical size determined by the Gibbs–Thomson effect, a well-known thermodynamic principle. At this critical size, the free energy change goes through a maximum that defines an energy barrier to island formation. The height of the free energy barrier decreases with increasing undersaturation and increases with increasing interfacial energy of the newly created surface (i.e., the edge of the island).

At sufficiently low undersaturation, the free energy barrier becomes too high for vacancy island nucleation to occur on a time scale that is competitive with the other processes. Dislocations, although few in number, then provide the dominant source of steps. The step density of etch pits at dislocations also depends on interfacial energy and undersaturation. At very low undersaturations, step density drops below the natural roughness of the crystal surface including the crystal edges, which are always a source of steps because they are rounded due to free energy minimization. Dissolution then is dominated by retreat of these preexisting steps.

To test these models for the dissolution of minerals, we generalize the original growth equations so that they describe both growth and dissolution for a wide range of saturations.

Dissolution at Dislocation. Regardless of the step source, the surface normal growth or retreat rate R of a crystal can be expressed as

$$R = \frac{h\nu}{\lambda}, \quad [3]$$

where h = step height, λ = step spacing, and ν = speed of a moving step. Both R and ν are negative for dissolution. Similarly, regardless of the step source, the ν in Eq. 3 depends on solution concentration according to the relation (8, 12)

$$\nu = \omega\beta(C - C_e) = \omega\beta C_e(\Omega - 1), \quad [4]$$

where β is the step kinetic coefficient ($\text{cm}\cdot\text{s}^{-1}$). Because β depends only on step direction and not the source of the steps, the determining factor for which step source dominates is the step spacing, λ .

Classical crystal growth theory states that there is a critical negatively free energy, ΔG_{Crit} , beyond which the line defects would expand continuously and become an etch pit (13–16). This relation is given by

$$\Delta G_{\text{Crit}}^d = -\frac{2\pi^2\alpha^2\omega}{\mu b^2}, \quad [5]$$

where α is the interfacial free energy, ω is the molecular volume of a molecule in the crystal, μ is the bulk shear modulus, and b is a Burgers vector. This critical value represents the activation energy barrier for the formation of an etch pit at a dislocation. The height of the activation energy barrier depends on the nature of the crystal (e.g., interfacial free energy and its Burgers vector) and is independent of solution undersaturation. Note that for an edge dislocation in quartz, the equation still applies because Poisson's ratio for quartz is small (0.077) (15).

When dissolution occurs at a dislocation, λ is related to the critical size r_c and the perimeter of the dislocation source P by

$$\lambda = \frac{8r_c + P}{m} \text{ with } r_c = \frac{\omega\alpha}{kT|\sigma|}, \quad [6]$$

where m = number of elementary steps, k = Boltzmann constant, T = temperature, and α = interfacial free energy associated with the step edge created at a pit, henceforth called “step edge energy.” By substituting Eqs. 4 and 6 into Eq. 3 and rewriting in the form of $\log|-R|$ vs. Ω to conform to the conventional method of presenting mineral dissolution data (as in Fig. 1a), we obtain the surface normal dissolution rate at a dislocation R_d as a function of undersaturation

$$\log|-R_d| = \log\left[\frac{A_1(1 - \Omega)|\ln\Omega|}{1 + A_2|\ln\Omega|}\right], \quad A_1 = \frac{mh\beta C_e kT}{8\alpha},$$

$$A_2 = \frac{PkT}{8\omega\alpha}. \quad [7]$$

Eq. 7 has properties that show the physical basis of the dissolution plateau and also shows the link to macroscopic rate laws. This function diverges negatively as Ω approaches 1, rises rapidly as Ω decreases, transitions to a plateau region of low slope near $\Omega = \exp(-1/A_2)$, and reaches a finite value as Ω goes to zero (note that plotting the data in this form accentuates the plateau). This result is qualitatively in agreement with quartz dissolution rates in pure H_2O . There are two additional effects that need to be considered. First, at very small Ω , step spacing becomes so close that the relationship in Eq. 4 is no longer valid because overlap in the diffusion fields for adjacent steps weakens the dependence on Ω (17). This effect accentuates the dissolution plateau by further reducing the slope. The second effect becomes important as Ω

approaches 1 where step spacing at dislocation sources, which varies as $1/\Omega$, becomes larger than the average step spacing of the initial crystal surface and/or the steps retreating from the crystal's edges, λ_0 . In addition, there is a critical energy barrier to etch pit formation. In this case, the step spacing also is given by λ_0 . Combining Eqs. 3 and 4, the dissolution rate becomes

$$-R = k_+(1 - \Omega), \quad k_+ = \frac{\omega\beta h C_e}{\lambda}. \quad [8]$$

This equation is of the form used to describe macroscopic dissolution rate data within standard transition state theory (5, 7) for the kinetics of a pseudo-first-order reaction. Here, we have related the macroscopic rate coefficient k_+ to the microscopic kinetic coefficient β of elementary step motion. As Fig. 1b shows, the near-equilibrium dissolution data do indeed exhibit a linear dependence on Ω . As a result, the electrolyte effect on relative dissolution rate becomes constant, whereas the absolute differences diminish to zero as the two curves converge to equilibrium ($\Omega = 1$). From a fit to the data we estimate k_+ to be $1.1 \pm 0.2 \times 10^{-8}$ and $5.1 \pm 1.2 \times 10^{-8} \text{ mol}\cdot\text{m}^{-2}\cdot\text{s}^{-1}$ for dissolution in the absence and presence of electrolytes, respectively.

Independent evidence for a transition from step retreat to dislocation-controlled dissolution at these conditions is found in the AFM images of the (100) quartz surfaces. Samples treated in solutions without salts at high driving force ($\Omega = 0.1$) reveal irregularly spaced etch pits having large dimensions of $\approx 4,000 \times 10,000 \text{ nm}$ (Fig. 2, ①). The sloping sides of these features merge with pointed bottoms, thus indicating that they arise from dislocation defects in the mineral (18). The prevalence of these etch structures concurs with earlier studies citing the importance of dislocation defects in controlling silicate dissolution at small values of Ω (15).

The complementary AFM images of quartz surfaces exposed to very near-equilibrium conditions ($\Omega = 0.90$) in CaCl_2 solutions confirm that dissolution occurs through a simple step retreat process by showing surfaces comprised of multiple straight-edged steps without evidence of etch pits (Fig. 2, ④). Note that these experiments purposefully used CaCl_2 solutions, which, as we show below, increase rates and probabilities of pit formation. We infer, therefore, that dissolution in solutions without electrolytes in these near-equilibrium solutions also proceeds by simple step retreat. At conditions where the driving force needed to initiate dissolution at dislocation defects is exceeded, our AFM observations reinforce the conclusion that total rate is governed by density of step edges.

Dissolution by Nucleation of Vacancy Islands. To explain the differences in the data obtained with and without salts in Fig. 1a, we now consider dissolution by etch pit nucleation at vacancy islands. The general expression for dissolution or growth by nucleation processes is based on the assumption that the free energy barrier to initiating a vacancy or adatom island, respectively, from a perfect surface, ΔG_{Crit}^n , is given by (9)

$$\Delta G_{\text{Crit}}^n = -\frac{\pi\alpha^2\omega h}{kT \ln \Omega}. \quad [9]$$

Eq. 9 shows that the barrier to formation of vacancy islands by 2D nucleation depends on solution undersaturation, in contrast to the energy barrier for etch pits formed at dislocations (Eq. 5). Hence, as the undersaturation increases, the energy barrier to nucleation must decrease.

When growth or dissolution occurs at a smooth face through 2D nucleation, the normal growth or dissolution rate (R_n) of the face due to formation of 2D nuclei at a rate of J is expressed as (8, 18)

$$|R_n| = h\nu^{2/3}J^{1/3}, \quad [10]$$

where the steady-state nucleation rate, J , is given by (9)

Fig. 2. AFM images of representative (100) surfaces of quartz exposed to four different solution chemistries for equivalent extents of reaction show the different dissolution processes across driving force and solution chemistry. (Scale bar: 1 μm in all images.) ① When $\Omega = 0.10$ in H_2O , surfaces are dominated by large etch pits with sloping sides that converge at dislocation sources. Pits are separated by relatively flat regions on the surface. ② For conditions where $\Omega = 0.10$ and the solution contains 0.0167 M CaCl_2 , the surface is covered with a high density of small pits with flat bottoms and with flanks that are 25% steeper than those measured for pits in ①. ③ At the intermediate driving force of $\Omega = 0.65$ in a salt solution of 0.0167 M CaCl_2 , a mixture of larger and smaller flat bottom pits form across the surface. ④ At a low driving force of $\Omega = 0.90$ in 0.0167 M CaCl_2 , the surface shows only straight-edged steps with no evidence of pitting.

$$J = |\sigma|^{1/2} n_s a h C_e \beta \exp\left(-\frac{\pi \alpha^2 \omega h}{(\mathbf{k}T)^2} \left| \frac{1}{\sigma} \right| \right), \quad [11]$$

where a is the lattice spacing and n_s is the density of nucleation sites, which in turn is proportional to $\exp(-E_b/\mathbf{k}T)$ where E_b is the kinetic barrier to etch pit formation associated with removal of atoms from the surface layer. Note that Eq. 11 shows that the nucleation process takes over because of the strong exponential dependence of rate on saturation state in contrast to the weak dependence that comes from Eq. 4. By substituting Eqs. 4 and 11 into Eq. 10, we rewrite Eq. 10 into a form that is linear in $1/\sigma$

$$\ln\left(\frac{|R_n|}{(\Omega - 1)^{2/3} |\sigma|^{1/6}}\right) = \ln(h\beta C_e (\omega^2 h n_s a)^{1/3}) - \frac{\pi \alpha^2 \omega h}{3(\mathbf{k}T)^2} \left| \frac{1}{\sigma} \right|. \quad [12a]$$

To derive an equivalent expression for dissolution at dislocations we rewrite Eq. 7

$$\begin{aligned} \ln\left(\frac{|R_d|}{(\Omega - 1)^{2/3} |\sigma|^{1/6}}\right) &= \ln\left(\frac{\omega \beta C_e m h}{P}\right) + \ln\left((\Omega - 1)^{1/3} \left| \frac{1}{\sigma} \right|^{1/6}\right) \\ &\quad - \ln\left(1 + 8\left(\frac{\omega \alpha}{P \mathbf{k}T}\right) \left| \frac{1}{\sigma} \right| \right). \end{aligned} \quad [12b]$$

Although this expression is no longer linear in $1/\sigma$, it allows us to make a direct comparison with Eq. 12a. The slopes of Eqs. 12a and 12b yield the step edge free energy, α , that corresponds to dissolution or growth by nucleation and dislocation processes, respectively. However, these energies are not those of the perfect crystal surface. Rather they are associated with the region of the crystal in the vicinity of the dislocation and/or impurity. Consequently, they are expected to be far less than that of the perfect crystal surface.

Applying Eq. 12a to the dissolution rate measurements collected in CaCl_2 and NaCl solutions results in two linear trends (Fig. 3b and c). A similar result also was documented for the dependence of growth on supersaturation in both inorganic and macromolecular systems (9, 19, 20). The region of steep slope found for growth at far-from-equilibrium conditions was postulated to correspond to the homogenous nucleation of adatom islands, whereas the region of shallow slope corresponds to islands nucleated at defects such as impurity atoms (9, 19, 20). Images ② and ③ in Fig. 2 confirm that dissolution features show the analogous nucleation of vacancy islands, and comparison with image ① in Fig. 2 shows that these structures contrast sharply with those produced in the absence of electrolytes; instead of exhibiting large, widely spaced, pointed-bottom pits, the (100) surfaces treated with solutions at $\Omega = 0.1$ that also contained CaCl_2 display a very high density of small etch pits with typical sizes of $250 \times 600 \text{ nm}$.

On surfaces etched under conditions corresponding to the region of steeper slope in Fig. 3b, the small, uniform size and distribution of pits across the surface indicate that they are the result of homogeneous 2D nucleation of vacancy islands (Fig. 2, ②). As such, they are continuously regenerated as the surface retreats. Comparisons of images ① and ② in Fig. 2 show that the physical basis for the salt effect arises through a transition from dissolution controlled by the population of dislocation defects to 2D nucleation of vacancy islands. As shown in Eqs. 11 and 12a, the data do not allow us to determine whether the source of this transition is from a reduction in the step edge free energy associated with the free energy barrier to stabilizing a pit or a reduction in the kinetic barrier, E_b , to removing atoms from the surface to initiate a pit, which manifests itself in n_s . Moreover, this physical model provides no information about the chemical source of either reduction. The calculated free energy barriers to dissolution by the 2D process are 61 ± 6 and $79 \pm 14 \text{ mJ/m}^2$ for NaCl and CaCl_2 solutions, respectively (see Table 2, which is published as supporting information on the PNAS web site).

The nucleation model also fits rates measured at the intermediate driving force to exhibit a linear trend of lower slope (Fig. 3b and c). This result corresponds to the growth regime in which Malkin and others (9, 19, 20) postulated that nucleation occurred preferentially at impurity defects. In this “defect-assisted” model, impurities induce localized strain to give lower free energy barriers than for 2D nucleation at a perfect surface. This explanation for growth is consistent with our dissolution data. The surface morphology, as seen in image ③ in Fig. 2 at $\Omega = 0.65$, shows the dominance of widely spaced, larger etch pits ($\approx 400 \times 1,300 \text{ nm}$) surrounded by smaller etch pits. The former are the pits that nucleate at defect sites. The latter are the homogeneously nucleating pits that grow in number until they completely dominate at high undersaturation (Fig. 2, ②). Fitting rates measured in CaCl_2 and NaCl solutions for conditions of region ③ with Eq. 12a indeed leads to a linear dependence and lower step edge energies. Our estimates of step edge energy for the CaCl_2 and NaCl solutions give values of 32 ± 10 and $18 \pm 8 \text{ mJ/m}^2$, respectively, for region ③.

To extract the step edge energy for dislocation sources, Eq. 12b is fitted to the rate measurements obtained for solutions with $\Omega < 0.85$ in solutions without electrolytes (region ① of Fig. 1a). The fit to the data (Fig. 3a) yields β values of $\approx 1 \times 10^{-6} \text{ cm/s}$ and $\alpha = 16.2 \pm 5 \text{ mJ}\cdot\text{m}^{-2}$. These estimates are specific to quartz at 200°C without electrolytes where the chemical potential conditions favor dissolution at dislocation defects. As one expects from the theory,

Fig. 3. Mechanistic models describe the dependence of dissolution rate on the driving force of undersaturation for measured rates of quartz and previously reported rates of aluminosilicate dissolution. (a) Dislocation model (Eq. 12b) predicts the behavior of quartz dissolution rate in the absence of electrolytes. (b) In contrast, dependence of quartz dissolution rate on undersaturation in 0.0167 M CaCl₂ solutions is predicted by the nucleation model (Eq. 12a). (c) Again, nucleation model fits quartz dissolution behavior in 0.05 M NaCl. (d) The lower temperature measurements of kaolinite dissolution rate at 80°C show a dependence on driving force that is predicted by the dislocation model. (e) In contrast, the markedly different dependence of kaolinite dissolution rate on driving force at 150°C is predicted by the nucleation model. The nucleation model describes data reported at acidic and circumneutral pH. (f) Reported rates of K-feldspar dissolution measured at 150°C and pH 9 also exhibit a dependence on undersaturation that is predicted by the nucleation model.

this direct estimate of quartz step edge energy is quite low compared with the macroscopic interfacial free energy estimated as $120 \text{ mJ}\cdot\text{m}^{-2}$ for 25°C (21) and $280 \text{ mJ}\cdot\text{m}^{-2}$ at 300°C (15). More significantly, it is also substantially lower than that for nucleation of vacancy islands either at homogenous or impurity sites. However, once these latter barriers are overcome, the measured rates are faster because the total number of pits, and therefore the total amount of step edge, or roughness, is far greater.

Nucleation Theory also Explains Silicate Dissolution Kinetics. Our success in applying nucleation rate theory to quartz dissolution leads us to test dissolution-rate data for silicate minerals. The complex rate data reported for the major rock-forming silicate, K-feldspar (22), appears to also obey nucleation rate theory (Fig.

3f) through the same processes that govern quartz dissolution in salt solutions (compare Fig. 3 b and c). The evidence suggests that, for decreasing driving force, the dominant dissolution process for this aluminosilicate also undergoes a transition from the homogeneous nucleation of vacancy islands to nucleation at impurity sites with step edge energies of 30 ± 4 and 8 ± 4 , respectively, for the conditions of the experiments.

We also find that nucleation theory reconciles the origin of different dependencies of kaolinite dissolution rates on driving force. To conduct this analysis, we use published experimental dissolution rates for kaolinite dissolution and growth measured at 80°C and 150°C (6, 23). By fitting these two data sets to the nucleation rate model, we show that the 150°C data fit the rate model for dissolution by 2D nucleation homogeneously and at

Fig. 4. Published kinetic data for kaolinite dissolution and growth give a test of the mechanistic models for both growth and dissolution. The theories predict the distinct differences in the dependence of dissolution and growth rates on undersaturation and supersaturation, respectively, that are reported. (a) The dislocation model, Eq. 12b, describes the dependence of reaction rates of growth and dissolution on positive and negative driving force, respectively, at 80°C. (b) Because of the exponential dependence of nucleation rate, J , on temperature, Eq. 11, a transition to dissolution and growth rates by surface nucleation processes occurs to give rate behavior described by the 2D nucleation model, Eq. 12a.

impurity defects to give surface energies of 23 ± 2 and 4 ± 2 mJ/m² at high and low driving force, respectively (Fig. 3e). In contrast, the rates measured at 80°C exhibit behavior predicted by the dislocation defect model (Fig. 3d). For this lower-temperature condition, we estimate $\alpha = 2.6 \pm 0.4$ mJ/m² and $\beta = \approx 2 \times 10^{-8}$ cm/s. Comparisons of these values show that the lower interfacial energy measured for the dislocation-driven dissolution is consistent with the theoretical model, but these differences alone do not account for the dramatic difference in behavior at these two temperatures. The true source of this difference is easy to understand from Eqs. 7 and 12a. R_d is weaker than linear in T , whereas R_n has an exponential dependence. At low T , R_d dominates, but as T increases, R_n quickly becomes greater. We conclude, therefore, that these kaolinite data sets are not at all inconsistent; rather, they exhibit a predictable thermally activated transition in the dominant dissolution mechanism.

Several insights to kinetic controls on mineral dissolution arise from our analyses of these aluminosilicates. First, the silicate minerals we tested are able to undergo dissolution by 2D nucleation at hydrothermal temperatures in pure solutions at moderate values of Ω , whereas quartz requires the presence of salts and far-from-equilibrium conditions to induce dissolution by this process. This difference can be understood from the lower value of α for silicate minerals, which allows dissolution by 2D nucleation without salts: no further change in mechanism occurs when salts are added. This finding explains why rates of silicate dissolution are not enhanced (4) when electrolytes are introduced. Second, the three mineral systems that we tested indicate that 2D nucleation dominates rates measured at higher temperatures of 150–200°C. In contrast, the 80°C data for kaolinite is predicted by the dislocation defect model. This sharp temperature-dependent change in mechanism suggests that the practice of extrapolating high temperature data to the ambient temperatures of earth surface environments may greatly overpredict rates of dissolution under circumstances where the extrapolation comes from rates driven by 2D nucleation. The lesson from this analysis is that one needs to know the boundaries between the various dissolution regimes before extrapolating measured kinetics to different temperatures. Third, we show that pH, which has a strong control on silicate dissolution rate, does not alter this behavior. Data reported for kaolinite at both pH 2 and 7.8 show that temperature drives the dependence of rate on saturation state.

Finally, we test the ability of the general forms of this theory given by Eqs. 12a and 12b to predict the dependence of kaolinite dissolution and growth on saturation state and temperature. By using reported rates for kaolinite at 80°C (6), Fig. 4a shows that dissolution and growth obey Eq. 12b. However, rates of growth and dissolution at 150°C (23) appear to be dominated by 2D and impurity-assisted nucleation processes at large and small excursions from equilibrium, respectively (Fig. 4b), according to Eq. 12a. Application of these relations again shows that, although the values of the material-dependent parameters α , β , and E_b will differ, the surface processes that hold for growth are directly analogous to those active during dissolution.

Broad Implications for Other Families of Crystalline Materials. Recent observations reported in the literature suggest that the nucleation model presented in this work also may predict the dissolution rates of the sparingly soluble salts. This finding hints at the possibility that the mechanistic model also will predict the rapid dissolution or “demineralization” of biological materials under some conditions. For example, brushite (CaHPO₄·2H₂O) demineralization results in “polypit” formation on the surface (24, 25). Similarly, a study of barite (BaSO₄) dissolution at high ionic strength showed 2D nucleation features (26). More recently, nanoscale observations of calcite (CaCO₃) dissolution across driving force found that surfaces undergo the same transitions in “dissolution modes” that change from retreat of steps, to opening and dissolution on dislocation etch pits, to the formation of 2D and defect-assisted nuclei (27). Although qualitative, the observations in these studies suggest that, as would be explained by the model, dissolution of sparingly soluble salts can be controlled by nucleation processes. This result is predicted with the mechanistic model because the relatively lower energy barriers to dissolution of these salts would allow a transition by 2D nucleation without the thermal activation required by the covalently bonded quartz and silicates.

The successes of classical growth theory in explaining the dissolution kinetics of minerals with properties spanning the covalent to ionic chemistries suggest it may become possible to predict the dependence of dissolution and corrosion on undersaturation and temperature for a large variety of minerals and crystalline materials. However, a number of questions are still unanswered. First, during dissolution, step splitting and retreat from crystal edges leads to the rounding of facet edges, but it is unclear what the contribution of this process is to the overall dissolution rate. Given sufficient time, it seems that these steps must retreat across the full diameter of a crystallite, but no evidence for these steps is seen in Fig. 2. Second, the step density and step speed will always determine the dissolution rate. Yet comparison of step densities for dislocation pits and etch pits in images ① and ② of Fig. 2, respectively, does not show an increase of the magnitude expected from the rate measurements. Moreover, the flat areas between dissolution pits in both cases show that, even at steady state, step retreat near the top of the pits must exceed that within the pits (28). Finally, although the model can be used to predict the dependence of rates on saturation state and temperature, without independent knowledge of materials parameters such as α , it cannot predict absolute dissolution rates. Moreover these parameters are likely to be largely unknown in natural systems. Consequently, despite the unifying and intuitive view of growth and dissolution provided by this model, there is much to be done to develop and test its concepts.

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Table 2. Summary of constants used to estimate step edge free energies, α , and kinetic coefficients, β , for quartz, feldspar, and kaolinite

Mineral	Solution*	Constants				Dislocation model (Eq. 12b)		Nucleation model (Eq. 12a)	
		Temp, °C	h , Å	ω , cm ³	$mh^\dagger$, Å	β , cm/s	$\alpha_{\text{dislocation}}$, mJ/m ²	$\alpha_{\text{homogeneous}}$, mJ/m ²	$\alpha_{\text{defect assisted}}$, mJ/m ²
Quartz	H ₂ O	200	4.33	3.77×10^{-23}	4.91	$\sim 1 \times 10^{-6}$	16.2 ± 5	—	—
Quartz	0.0167 M CaCl ₂	200	4.33	3.77×10^{-23}		—	—	79 ± 14	32 ± 10
Quartz	0.05 M NaCl	200	4.33	3.77×10^{-23}		—	—	61 ± 6	18 ± 8
Feldspar [‡]	KCl/KOH, pH 9	150	7.22	1.80×10^{-22}		—	—	30 ± 4	8 ± 4
Kaolinite [§]	HClO ₄ /NaOH, pH 3	80	7.37	1.65×10^{-22}	7.37	$\sim 2 \times 10^{-8}$	2.6 ± 0.4	—	—
Kaolinite [¶]	HCl, pH 2	150	7.37	1.65×10^{-22}		—	—	23 ± 2	4 ± 2
Kaolinite [¶]	NH ₄ Cl/NH ₄ OH, pH 7.8	150	7.37	1.65×10^{-22}		—	—	24 ± 2	7 ± 3

*Note that the aqueous solutions also contain dissolved aqueous silica and (as applicable) stoichiometric amounts of aluminum.

[†]The Burgers vector, $b = mh$, is used to estimate the perimeter, P , in Eq. 12b by the relation $2\pi r_h$. Values of r_h for quartz and kaolinite are $1.25b$ and $2.5b$, respectively (16). No value is reported for K-feldspar because only the dislocation model requires b .

[‡]Dissolution rate data from ref. 22 using $\log K_{\text{sp}} = -15.24$ at 150°C.

[§]Dissolution rate data from ref. 6 using $\log K_{\text{sp}} = 3.75$ for pH = 3, $T = 80^\circ\text{C}$.

[¶]Dissolution rate from ref. 23 using $\log K_{\text{sp}} = -4.00$ (pH 2) and $\log K_{\text{sp}} = -7.45$ (pH 7.8) at 150°C.

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IMMUNOLOGY

An Inflammatory Lineage

Helper CD4⁺ T (T_H) cells are traditionally divided into two principal lineages: interleukin-4 (IL-4)/IL-5–producing T_H2 cells, which are associated with allergic and antiparasitic responses, and T_H1 cells that produce inflammatory cytokines, principally interferon- γ (INF- γ). However, the expression of the cytokine IL-17 by a relatively small subset of CD4⁺ T cells and its association with inflammation has suggested that this may define a T_H1 sublineage.

Now, Harrington *et al.* and Park *et al.* provide evidence that IL-17–producing CD4⁺ T cells may represent a distinct T-helper population altogether, the development of which is coordinately regulated with those of T_H1 and T_H2 cells. Both studies confirmed the dependence of IL-17 expression on signaling through the receptor for the cytokine IL-23 and demonstrated that this was independent of the signals and transcriptional pathways responsible for IFN- γ and IL-4 production. Furthermore, both of these T-helper cytokines were found to inhibit IL-17 expression in naïve T cells—as opposed to differentiated IL-17⁺ T cells—suggesting a dominant role in cross-regulation during early T cell priming. Given the clear association of IL-17 with tissue inflammatory responses, the strict management of T_H17 cell differentiation may represent a central checkpoint in preventing immune pathologies such as those seen in autoimmune diseases. — SJS

Nat. Immunol. 6, 1123; 1133 (2005).

Lung inflammation induced by overexpression of IL-17 (lower row), with increases in mucus production (arrows, left) and collagen deposition (arrow, right) in bronchioles.

equal to the half-life for ²³⁹Pu decay. Fortunately, the soil bacterium *Pseudomonas pavonaceae* expresses the enzyme CaaD, which Horvat and Wolfenden show accelerates hydrolysis, yielding malonate semialdehyde through addition of water and loss of HCl, by a factor of 10¹². They argue that this impressive rate enhancement is due largely to chemical transformations taking place in the active site (as opposed to substrate binding or product release) and that CaaD appears to be a considerably more proficient enzyme than its structural cousin 4-oxalocrotonate tautomerase, all of which provides support for the proposal that the degradation of 3-chloroacrylate may be a recently acquired activity of a relatively ancient and catalytically sophisticated enzyme. — GJC

Proc. Natl. Acad. Sci. U.S.A. 102, 16199 (2005).

GEOCHEMISTRY

Reversing Crystal Growth

Much of the chemistry and dynamics of Earth's surface depends on the dissolution of minerals: It determines the composition of soils, rivers, and oceans and affects the amounts of major gases, such as CO₂, in the atmosphere. Rapid dissolution weakens rocks, facilitating erosion, and dissolution and corrosion are critical in evaluating the performance of engineered structures. Various data have implied that the dissolution rates of many minerals are complex functions, depending subtly on interacting waters, for example.

Dove *et al.* show, both theoretically and through experi-

CLIMATE SCIENCE

Warmer and Drier

One effect that is expected to accompany global warming is the occurrence of more intense and more frequent droughts. Although it is known that protracted drought increases tree mortality, the response of forests on regional or continental scales to the kind of warmer drought that may occur in the future is poorly understood.

Breshears *et al.* examined the impact of recent drought on piñon pine trees in western North America, focusing on the relationships between tree die-off, temperature, and rainfall. They found that the 2000–2003 drought was not as dry as the previous one of 1953–1956, but that it occurred during a warmer period and hence might illustrate drought effects in the future. Their analysis shows that the recent drought caused a rapid

regional-scale loss of overstory trees mainly due to infestation by bark beetles, outbreaks of which are commonly caused by water stress; whereas the 1950s drought affected mainly older trees, the 2000s drought killed trees of all ages. Similar widespread drought in this century could cause large changes in carbon storage and dynamics, in fluxes of near-ground solar radiation, and in patterns of runoff and

Changes in the normalized difference vegetation index (green, no change; red, largest decrease) in the southwestern US.

erosion, as well as alter microclimate feedbacks between the land and atmosphere and reduce the production of piñon nuts, an important food source for a number of species of birds, small mammals, and local people. — HJS

Proc. Natl. Acad. Sci. U.S.A. 102, 15144 (2005).

BIOCHEMISTRY

New Activity, Old Enzyme

Ever since we realized that chemicals introduced into the environment for the control of agricultural pests can persist for uncomfortably long periods, there has been an interest in microbes that are able to adapt to living off of (metabolizing) these synthetic carbon sources. In the case of the nematocide 1,3-dichloropropene, its degradation product, *trans*-3-chloroacrylic acid, undergoes hydrolytic decomposition with a half-life of 24,000 years at 19°C, roughly

ments, that for quartz, and likely for other silicate minerals, well-developed theories of crystal nucleation and growth can be used to understand dissolution. Nucleation theory involves four parameters: temperature, oversaturation, and two parameters that describe the energy and kinetics associated with a step on a growing crystal. The authors derive the analogous equations for dissolution at dislocations and vacancies, and show that the theory fits well with experimental data for quartz, feldspar, and a common clay mineral, dissolving in waters under a range of pH and salt conditions. If the result holds across a full range of minerals, it would allow the prediction of dissolution and corrosion under a variety of conditions and temperatures. — BH

Proc. Natl. Acad. Sci. U.S.A. 102, 15357 (2005).

APPLIED PHYSICS

Patterns of Light

Polymers have found use in the fabrication of optoelectronic and magnetic devices and as inexpensive, flexible, and lightweight templating materials. Patterns are created through the solvent or by thermally driven phase separation of a blend of homopolymers or block copolymers. One problem with using homopolymers is that it is difficult to

create large areas that are defect-free yet retain precise patterning on a much smaller scale. Block copolymers are better for achieving this, but changes in the pattern can require the synthesis of a new copolymer.

Travasso *et al.* describe an alternative method for creating materials that are spatially patterned on the submicrometer scale and are defect-free on the millimeter to centimeter scale. They consider a ternary A/B/C blend of immiscible polymers. Polymers A and B are chosen so

Ternary A/B/C blends (blue/red/green)

that the extent to which they interact or separate can be tuned by exposure to light. Initially, a uniform light source is used to create a homogenous mixture of A and B. By rastering over the sample with a higher-intensity secondary beam, defects in the local pattern can be annealed out. Polymer C is chosen to migrate to areas illuminated by the higher-intensity light. Thus, it is possible to write regions of polymer C onto a spatially patterned AB film. — MSL

Langmuir 10.1021/la052511a (2005).

HIGHLIGHTED IN SCIENCE'S SIGNAL TRANSDUCTION KNOWLEDGE ENVIRONMENT

Bacterial Pheromone for Sex and Abstinence

Bacteria can transfer DNA through conjugation, and the transfer of these extrachromosomal elements contributes to virulence and antibiotic resistance. Chandler *et al.* report that in *Enterococcus faecalis*, a mammalian pathogen, the same pheromone that stimulates a donor bacterium to initiate conjugation with a plasmid-free recipient is also produced by the donor itself and regulates its sensitivity to the recipient-produced pheromone. The bacterial chromosome encodes the pheromone (cCF10), so both donor and recipient can produce this molecule; to prevent conjugation with other donors, donor cells have two mechanisms for suppressing the response to the endogenously produced pheromone. One of the conjugation inhibitors is a secreted inhibitor protein, iCF10, which binds and sequesters secreted cCF10, and another is the membrane protein PrgY, which degrades or binds cCF10 as it is released. Using mutant bacterial strains that lacked functional cCF10, Chandler *et al.* show that cCF10 produced by the donor cells stimulates the production of iCF10. Donor cells grown in human plasma or in vivo also produce the plasmid-encoded aggregation factor Asc10, which contributes to cellular invasion and virulence of the bacteria. Albumin was identified as the plasma protein that bound iCF10, thereby shifting the balance between iCF10 and cCF10, allowing self-induction of the conjugation genes, including the one encoding Asc10. — NRG

Proc. Natl. Acad. Sci. U.S.A. 102, 15617 (2005).

MECHANISMS OF CLASSICAL CRYSTAL GROWTH THEORY EXPLAIN QUARTZ AND SILICATE DISSOLUTION BEHAVIOR

(PNAS 102, 15357-15362)

Patricia M. Dove, Nizhou Han and James J. De Yoreo

Aqueous fluids play a crucial role in mineral weathering and transport in sediments, as well as in fluid-rock interaction deeper in the Earth's crust. For decades researchers have sought general descriptions of mineral dissolution kinetics as a means to

quantify and predict behavior over time spans greatly exceeding those accessible in the laboratory. However, a relationship incorporating thermodynamic variables and time that "works" over a range in saturation level and temperature has been elusive—even for a single mineral under laboratory conditions.

In a study published recently in the *Proceedings of the National Academy of Sciences*, Patricia Dove and Nizhou Han at Virginia Tech and their colleague Jim De Yoreo at Lawrence Livermore National Laboratory have shown that mineral *dissolution* can be understood through the same mechanistic theory of nucleation developed previously to describe

pure quartz sand, in which they measured the dependence of dissolution rate on undersaturation. Complementary AFM observations of the steady state surfaces that developed on natural faces showed that rates conform to model predictions over a wide range of thermodynamic conditions. They also showed that the "salt effect," recognized almost 100 years ago, results from a transition in the dominant mechanism from dislocation- to nucleation-driven dissolution.

It turns out that the model also explains dissolution behavior previously reported for feldspar. It also reconciles apparently conflicting data sets for kaolinite dissolution at two different temperatures by showing the basis for a temperature-activated transition in the dissolution process. These differences suggest that the practice of extrapolating high-temperature data to ambient temperatures may over-predict rates of dissolution when the extrapolation comes from rates driven by etch-pit nucleation.

The researchers believe that their nucleation model may also predict dissolution rates of sparingly soluble salts, perhaps opening up the possibility to understand "demineralization" of biological materials under certain conditions.

Mechanisms of classical crystal growth theory explain quartz and silicate dissolution behavior (PNAS 102, 15357-15362) Patricia M. Dove, Nizhou Han and James J. De Yoreo

This article was picked by **Bruce Watson**.

mineral *growth*. By viewing dissolution as the formation of "negative crystals," the researchers were able to generalize the nucleation-rate equations to obtain a model that predicts progressive changes in the dissolution mechanism with degree of undersaturation—from step retreat to defect-controlled to homogeneous nucleation of etch pits. The underlying reason for the transitions is that the rate at which a crystal dissolves is controlled by the density of steps on the surface. Whichever process creates the greatest step density dominates the dissolution process.

Prof. Dove and her colleagues tested the model using a new set of experiments performed on

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