

Nanoscience Meets Geochemistry: Size-Dependent Reactivity of Hematite

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Doctor of Philosophy in Geosciences

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ABSTRACT

Recent studies have demonstrated that nanoscale crystalline iron oxide minerals are common in natural systems. The discipline of nanoscience suggests that these particles in the size range of approximately 1-50 nm will have properties that deviate from the bulk properties of the same material and that these properties will change as a function of particle size. This study begins to fill the void of corresponding experimental investigations that apply the principles of nanoscience to the geochemical reactivity of nanominerals.

The rate of $\text{Mn}^{2+}(\text{aq})$ oxidation on hematite with average diameters of 7.3 nm and 37 nm was measured in the presence of $\text{O}_2(\text{aq})$. In the pH range of 7-8, the surface area normalized rate was one to two orders of magnitude greater on the 7.3 nm average diameter particles. Based on the application of electron transfer theory, it is hypothesized that the particles with diameters less than approximately 10 nm have surface crystal chemical environments which distort the symmetry of the Mn^{2+} surface complex, reducing the energy required to reorganize the coordinated ligands after oxidation to Mn^{3+} .

Cu^{2+} , an analog for Mn^{3+} , was used to probe for the presence and nature of the proposed changes in surface structure. Cu^{2+} and Mn^{3+} show similar electronic structure changes in response to the surrounding crystal field due to their d-electron configurations and Jahn-Teller coordinative distortions. Batch sorption experiments on hematite nanoparticles revealed a shift in the pH-dependent adsorption of $\text{Cu}^{2+}(\text{aq})$. Specifically,

an affinity sequence of 7 nm > 25 nm = 88 nm was determined based on the shift of the 7 nm sorption edge to approximately 0.8 pH units lower than that for the 25 nm and 88 nm samples. These data support the hypothesis that unique binding sites exist on the 7 nm nanoparticles that are not significantly present on the larger particles.

The National Nanotechnology Initiative stresses the need to address the broader societal impacts of nanoscale research. This dissertation embraces this viewpoint through the development and inclusion of “Nano2Earth: Introducing Nanotechnology Through Investigations of Groundwater,” a curriculum which combines nanoscience with the Earth sciences for high school students.

Dedication

At the quantum level our universe can be seen as an indeterminate place, predictable in a statistical way only when you employ large enough numbers. Between that universe and a relatively predictable one where the passage of a single planet can be timed to a picosecond, other forces come into play. For the in-between universe where we find our daily lives, that which you believe is a dominant force. Your beliefs order the unfolding of daily events. If enough of us believe, a new thing can be made to exist. Belief structure creates a filter through which chaos is sifted into order.

- Frank Herbert

This dissertation is dedicated to all of those who believed in me, and by their believing made this possible. They include most of all my parents, brother, and Megan, and also very importantly Tom Wiersma (Robert L. Nickels Middle School), Prof. Michael A. Velbel (Michigan State University), and Prof. Michael F. Hochella, Jr. (Virginia Tech).

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Chapter 1 – Introduction

Nanoscience Meets Geochemistry

The scientific field of nanoscience explores how the properties of materials change as a function of size in the range of approximately 1-50 nm. These materials may include commonly studied phases such as metals and semiconductors, or materials that exist uniquely in this size range. Material properties change due to the evolution of the surface and electronic structure throughout this size range, until the material becomes “bulk-like” and will exhibit the electronic, conductive, thermal, thermodynamic, magnetic, mechanical, optical, and other properties that we otherwise commonly associate with that material.

The field of geochemistry is concerned with the distribution of elements in natural systems and the processes with cause elements to transform between chemical forms and chemical reservoirs. Much of this chemistry occurs on the Earth at the interfaces between the lithosphere, hydrosphere, biosphere, and atmosphere. In fact, at a fundamental level, much of the natural geochemistry of Earth (excluding the massive impact of human activity) is controlled by processes that occur on individual mineral, bacterial and plant root surfaces that are in contact with air and water.

Nanoscience meets geochemistry in the realization that nanoscale particles are common in natural systems. More relevant to this study, the application of transmission electron microscopy and other experimental techniques to natural materials has led to the discovery that *crystalline* nanominerals are common. Furthermore, nanoscience meets geochemistry in the study of how the size of the particle influences the geochemical reactivity of nanominerals found in natural systems. This study includes the first

application of nanoscience to size-dependent reactivity of common geochemical reactions with a common mineral.

Size-Dependent Reactivity of Hematite

Hematite ($\alpha\text{-Fe}_2\text{O}_3$) was chosen as a model compound for studies of size-dependent reactivity for several reasons. 1) Iron oxide minerals such as hematite are found ubiquitously on Earth and elsewhere in the solid components of the solar system. As the most abundant redox-active metal, iron participates in a wide variety of inorganic, biological, and photochemical processes. 2) Although hematite is not quite as abundant at the Earth's surface as goethite ($\alpha\text{-FeOOH}$), its semiconducting properties (i.e., its electronic structure) make it the most amenable of the ferric oxide minerals to study. Finally, several well-researched recipes for the synthesis of hematite nanoparticles exist in the literature. This is not the case for goethite.

Nano2Earth: Introducing Nanotechnology Through Investigations of Groundwater

The lead organization for nano-related research in the United States is the National Nanotechnology Initiative (NNI). The NNI has repeatedly stated that up to millions of workers trained in nanoscale science, technology, and engineering will be required within the next one to two decades. In addition, a central mission of the NNI is to inform the general public about the benefits of nano-related research and its enormous societal implications for the future.

Nano2Earth is a high school curriculum that was created to respond to this NNI mandate for public outreach. By introducing high-school age students to actual research

in and applications of nanoscale science and technology, Nano2Earth hopes to provide a mechanism to aid in the exposure of young people to the scientific fundamentals of nanoscience and technology. Based on the National Science Education Standards, the curriculum contains five lessons that may be used in totality or individually based on the interest of the teacher and the time available. Several weeks of class time would be required for the entire curriculum. Currently, the curriculum is continuing to undergo classroom testing while commercial publishers are considering the project for national distribution.

Structure of the Dissertation

This dissertation consists of two first-authored journal articles, as well as Nano2Earth, and an Appendix with two additional coauthored manuscripts. Chapter 2 “Testing geochemical reactivity as a function of mineral size: manganese oxidation on hematite nanoparticles” has been published in *Geochimica et Cosmochimica* (vol. 69, pg. 389-398, 2005) and appears courtesy of Elsevier Science, Ltd. Chapter 3, “Insights for size-dependent reactivity of hematite nanomineral surfaces through Cu^{2+} sorption” is in final stages of preparation and will be submitted shortly.

Chapter 4, “Nano2Earth: Introducing Nanotechnology Through Investigations of Groundwater” is the end product of a large-scale collaborative project. As part of a Nanoscale Interdisciplinary Research Teams grant from the National Science Foundation, we began a four-year long task of generating instructional materials appropriate to introduce nanoscale science and technology to high-school age students. A large team of approximately 25 people have worked on the project at different stages and in different

levels of participation. Critical to the project was the partnership between scientists and educators. Participating educators include Dr. George Glasson and graduate students from the Virginia Tech Department of Teaching and Learning, along with competitively selected high school teachers from nearby schools whose experience cuts across the science disciplines. Ellen Mathena and Mark Fortney of the Virginia Tech Department of Geosciences were crucial in formulating the final layout.

The Appendix contains two manuscripts in press. First is a work primarily performed by Isidoro Giorgio Lesci and his dissertation advisor Elisabetta Roveri from the University of Bologna, Italy. Several aspects of sample characterization were performed in collaboration with the NanoGeoscience and Technology Laboratory at Virginia Tech during the visit of I. Giorgio Lesci to Virginia Tech. The included manuscript, “Morphological and chemical-physical characterization of Fe doped synthetic chrysotile nanotubes” is in press with the journal *Advanced Functional Materials*. The second manuscript in the appendix, “Earth’s nano-compartment for toxic metals”, was an invited submission for the first author, Michael Hochella, to the new magazine *Elements*. Sponsored by several international geochemical and mineralogical societies, *Elements* highlights areas of current and exciting research of interest to all in the fields of geochemistry and mineralogy at a level to avoid discipline-specific jargon.

Chapter 2

A test of geochemical reactivity as a function of mineral size: manganese oxidation promoted by hematite nanoparticles

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ABSTRACT

$\text{Mn}^{2+}(\text{aq})$ oxidation as promoted by hematite in the presence of molecular oxygen has been studied as a function of hematite particle size. This system is a good candidate to serve as a test of the change of particle reactivity as a function of size due not only to its importance in Earth/environmental processes, but also because it involves electronic coupling between the hematite and adsorbed manganese. The properties of nanoscale hematite, including size quantization of the electronic structure and the relative proportions of terrace vs. edge/kink sites, are expected to change significantly with the particle size in this size range. Experimental results from this study suggest that the heterogeneous manganese oxidation rate is approximately one to one and a half orders of magnitude greater on hematite particles with an average diameter of 7.3 nm than with those having an average diameter of 37 nm, even when normalized to the surface areas of the particles. The acceleration of electron transfer rate for the reactions promoted by the smallest particles is rationalized in the framework of electron transfer theory. According to this theory, for a reaction such as heterogeneous Mn oxidation, the rate depends on three factors: the electronic coupling between initial and final electronic states, the substantial reorganization energy for solvent and coordinated ligands between initial and final states, and the free energy of reaction (corrected for work required to bring reactants together). The adsorbed Mn is electronically coupled with the solid during the electron transfer, and changes in the electronic structure of the solid would be expected to influence the rate. The Lewis base character of surface oxygen atoms increases as the electronic structure becomes quantized, which should allow increased coupling with adsorbed Mn. Finally, as demonstrated previously by in-situ AFM observations, the reaction proceeds most readily at topographic features that distort the octahedral Mn^{2+} coordination environment. This has the effect of lowering the reorganization

energy, which effectively controls the magnitude of the transition state barrier. Previous studies of <10 nm diameter hematite nanoparticles have demonstrated a decrease of symmetry in the average coordination environment of surface atoms, supporting the idea that smaller sizes should correspond to a decrease in reorganization energy.

1. INTRODUCTION

In recent years, geoscientists have become increasingly aware of the presence and novel role nanocrystalline materials play in Earth's geo/hydro/biosystems (Banfield and Navrotsky, 2001; Hochella, 2002a). Fundamental physics and chemistry suggest that the properties of these materials will change as a function of size in the nanoscale domain; this must have implications tied to geochemical reactivity. These implications are difficult to assess due to the lack of supporting experimental investigations.

The ability of solid surfaces, such as metal oxide mineral surfaces, to promote the oxidation of $\text{Mn}^{2+}(\text{aq})$ provides the opportunity to test the importance of nanoparticle size on an important geochemical process. Manganese oxidation is extremely slow in the absence of a promoter (Diem and Stumm, 1984). In many geological systems bacterially mediated oxidation dominates this process (e.g. Tebo and Ghirose, 1997; Tebo et al., 2004), while in others adsorption and reaction at surfaces influences Mn transformations (e.g. Hochella et al., in press a). As will be described in more detail, hematite surfaces donate electron density to adsorbed Mn^{2+} , encouraging reaction with O_2 . Size quantization effects should alter the electron density donating properties of the surface, causing the reactivity of nanoparticles to change as a function of size. In addition, the lower percentage of terrace sites on the smallest particles leads to an enhancement of the rate due to the geometric dependence of the hypothesized reaction mechanism.

The products of the Mn oxidation reaction, manganese oxide minerals, participate in a wide variety of environmental reactions. In soils and sediments they act as extremely efficient cation sorbents for metals such as Pb, Zn, and Cu (O'Reilly and Hochella, 2003; Hochella et al., in press a). They are also involved in heterogeneous redox transformations that influence the

fate and transport of contaminants such as chromium (Weaver and Hochella, 2002; Weaver et al., 2003) and arsenic (Nesbitt et al., 1998), organics such as pesticides and humic materials (Stone and Morgan, 1984; Nico et al., 2002), and radioactive materials leached from nuclear processing and storage facilities (Zachara, 1995; Fendorf et al., 1999).

1.1. Natural Iron Oxide Nanoparticles

Nanocrystalline ferrihydrite, goethite, schwertmannite, hematite, akagenite, and possibly other iron oxide phases are found in many geological environments. For example, Swartz et al. (1997) and Penn et al. (2001) show two cases where the reddish, supposedly amorphous material coating aquifer sand grains actually contains distinct ~5-10 nm goethite grains embedded in an Al-Si matrix. Other iron oxide nanoparticles are found in atmospheric dust particles (Anastasio and Martin, 2001), incipiently weathered soils (Bell et al., 1993), acid mine drainage effluent (Hochella et al., 1999; Jambor et al., 2000; Sullivan and Drever, 2001; Hochella, 2002a; Hochella, 2002b), oxisols (Fontes et al., 1992), uranium deposits (Utsunomiya and Ewing, 2003), bacterial surfaces (Banfield et al., 2000), metamorphic rutile (Banfield and Veblen, 1991), and probably the surface of Mars (Morris and Lauer, 1990; Morris, 1993).

It is difficult to evaluate the overall role of nanophase iron oxides in natural systems; the complexity of natural systems and the difficulties in sampling and observation present serious barriers to our understanding. Nevertheless, some clues are starting to emerge for oxide mineral nanoparticles in general. For example, it has been demonstrated that the ability of nanoparticles to adsorb low molecular weight organic acids exceeds predictions based solely on the surface area/volume ratio as extrapolated from results measured with larger particles of TiO₂ (Zhang, 1999) and manganese oxides (Nelson et al., 1999). The greater adsorption capacity and

resistance to gravitational settling of nanoparticles make them potentially extremely important in the transport and cycling of trace metals and contaminants (Hochella et al., 1999, in press (a,b)).

1.2. Properties of Nanoparticles

Nanoparticles are those solid materials having physical dimensions of around one nm to about 100 nm. Interest in this size domain has arisen partly due to the discovery that materials with these dimensions often have properties that are intermediate between those of molecular clusters and bulk materials. It has been widely appreciated that as the dimensions of a particle are reduced, a greater percentage of the atoms present exist on the surface. Geochemists and mineralogists have studied the effects of unsatisfied bonding at the surface and its consequences for structure (Waychunas, 2001), reactivity (Hochella et al., 1990), and the increasingly large contribution of the surface free energy to particle stability (Navrotsky, 2001). Electronic, magnetic, optical, and other material properties also progressively deviate from “bulk” behavior.

Perhaps the most exciting and technologically important types of nanomaterials with tremendous potential for commercial application are quantum wells, wires, and dots. These materials have electronic wavefunctions that are confined in one, two, and three dimensions, respectively (Hochella, 2002a). In particular, semiconductor quantum dots are those particles with semiconducting properties and electronic wavefunctions that are confined in all dimensions (Steigerwald and Brus, 1990; Wang and Herron, 1991; Weller, 1993; Alivisatos, 1996a; Alivisatos, 1996b). This “quantum confinement” refers to conduction band electrons which are delocalized throughout the boundaries of a particle and have altered energy levels as their wavelengths approach the dimensions of the box (the box being the potential field of the particle) (Fig. 1). Changing nanoparticle electronic behavior is also rationalized by “size quantization

effects” which describes changes in the distribution of the electronic density of states (DOS). Near the top of the valence band and the bottom of the conduction band, the DOS becomes discrete (especially at lower temperatures), which can be observed using various spectroscopies. The electronic structure is becoming increasingly quantized in the transition from continuous energy bands to discrete molecular states.

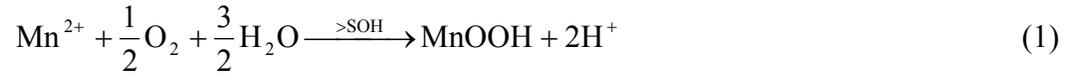
Few reviews have focused on oxides or insulating materials, although these exhibit size quantization effects as well (Noguera, 2001; Noguera et al., 2002). Changes in electron density have been predicted for oxides experiencing size effects, with the surface oxygen atoms becoming increasingly basic due to reductions in the Madelung energies for ultra-thin films and low-coordinated sites (Noguera et al., 2002).

Changes in the atomic surface structure are also related to changes in nanoparticle electronic structure. X-ray absorption spectroscopy studies of transition metal oxide nanoparticle structures as a function of size suggest a decrease in symmetry of the metal surface atoms as the particle size is reduced below 10 nm for anatase (Chen et al., 1997) and hematite (Chen et al., 2002; Zhang et al., 2003). These studies indicate that in vacuum the average coordination number of surface Fe atoms decreases; the corresponding nanoparticle surfaces in aqueous solution would retain octahedral coordination with oxygen due to the presence of water molecules, although the geometry of the coordination sphere would be distorted. Changes in the coordination environment of surface atoms can generate increased reactivity due to the sensitivity of the under- or oversaturation of available electron density to metal-oxygen bond distances (Bickmore et al., 2003). Recent studies of the hydrated hematite surface structure demonstrate the complexity of single-crystal hematite surface in aqueous solution (Liu et al., 1998; Eggleston et al., 2003; Trainor et al., 2004).

1.3. Manganese Oxidation and Kinetic Model

The homogenous oxidation of Mn^{2+} by O_2 proceeds extremely slowly at $\text{pH} < \sim 8.5$ (Diem and Stumm, 1984). When surfaces are available for Mn sorption, oxidation proceeds much faster. The oxygen atoms from dissociated hydroxyl groups on mineral surfaces are able to donate electron density to adsorbed Mn, encouraging the transfer of an electron from Mn^{2+} to O_2 in a manner analogous to the effect of hydrolysis on increasing metal ion oxygenation rates (Luther, 1990; Rosso and Morgan, 2002). Similar promotion of the reaction between adsorbed metals and O_2 has been observed for ferrous iron and the vanadyl ion (Stumm, 1988; Wehrli et al., 1989).

The overall reaction expected during the kinetic experiments in this study, using similar conditions, is (Junta and Hochella, 1994):



Nonenzymatic manganese oxidation has been modeled with a pseudo-first order general rate law:

$$-\frac{d[\text{Mn(II)}]}{dt} = \sum_{i=1}^3 k_i [\text{Mn(II)}] \quad (2)$$

where k_1 is the pseudo-first order homogeneous rate constant, k_2 is the pseudo-first order autocatalytic rate constant, and k_3 is the pseudo-first order heterogeneous rate constant. Each one of these rate constants is dependent on the experimental conditions as given by equations 3-5:

$$k_1 = k_{\text{hom}} [\text{OH}^-]^a [\text{O}_2] \quad (3)$$

$$k_2 = k_{\text{auto}} [\text{OH}^-]^b [\text{MnO}_x] [\text{O}_2] \quad (4)$$

$$k_3 = k_{\text{het}} [\text{OH}^-]^c [\text{Substrate}] [\text{O}_2] \quad (5)$$

where a , b , and c are typically found to be 1.5-3. All three reactions are expected to participate in parallel in the experiments described in this study. The homogenous rate is several orders of magnitude less and can be neglected (Diem and Stumm, 1984). The autocatalytic rate may begin to dominate as the reaction progresses, but the initial rates are dominated by k_{het} , as supported by AFM observations (Junta-Rosso et al., 1997).

2. MATERIALS AND METHODS

2.1. Hematite Synthesis

Hematite nanoparticles were synthesized by slowly dripping 60 mL of 1 M ferric nitrate solution into 750 mL of boiling ultrafiltered and doubly distilled MilliQ water (Mulvaney et al., 1988). After the drip solution was consumed, the nanoparticle suspension was removed from heat. Due to their mean diameter, product from this synthesis will be referred to as <7.3 nm>. For synthesizing larger hematite particles, a screw-cap bottle containing 500 mL of 0.002 M HCl was brought to 98°C in a vacuum oven and held at this temperature overnight. After brief removal from the oven, 4.04 g of $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ was added and the bottle was vigorously shaken. Immediately, the bottle was returned to the oven and held at 98°C for seven days. Again, due to the mean diameter of this product, it will be referred to as <37 nm>. After both synthesis suspensions were cooled overnight, they were dialyzed against MilliQ doubly distilled water until the conductivity of the dialysis water reached that of pure MilliQ, generally taking two to four days depending on the synthesis method. Suspensions were poured from the dialysis tubing (6,000-8,000 molecular weight cut off) into HDPE bottles for storage.

2.2. Transmission Electron Microscopy (TEM)

The products were observed in a Phillips EM 420T Scanning Transmission Electron Microscope operated in bright field mode at 100 KeV. Drops of the synthesis products were placed onto formvar-coated copper grids and allowed to evaporate. No further specimen preparation was necessary. Particle size analysis was done by observations of TEM negatives using a 10x magnifier with 0.1 mm divisions.

2.3. Atomic Force Microscopy (AFM)

Atomic Force Microscopy was accomplished using a Digital Instruments MultiMode AFM operated with a Nanoscope IIIa controller. Hematite suspensions were diluted with MilliQ water and dropped onto a Si wafer surface. After evaporation, the particles were imaged in air in Contact Mode with oxide-sharpened silicon nitride tips. Images were planefit offline, followed by a flattening routine and sometimes Gaussian noise reduction before image analysis.

2.4. Surface area

2.4.1. Geometric surface area

In this study, surface areas of nanoparticle suspensions were determined by estimation based on the geometry of the particles and their sizes recorded from TEM and AFM images. Particles from the <7.3 nm> sample are pseudo-hexagonal platelets. The geometric surface area was determined assuming the particles were hexagons with an extra area caused by the irregularity of the particle. The length:width ratio was measured and used to correct from the perfect hexagonal model. Despite the presence of rhombohedral particles in the <37 nm> sample, the same hexagonal platelet geometric model was used. The particle diameters were arranged into 0.5 nm and 5 nm histogram bins for the <7.3 nm> and <37 nm> samples, respectively. Mean thicknesses from AFM images were used for each histogram bin, as the thickness could not be accurately related to the particle diameter because of tip-sample interaction.

The total surface area is determined by summing over the entire histogram. Further manipulation was required to obtain the surface area of the particles in m²/g, as given in equation (6):

$$\text{surface area} \left(\frac{\text{m}^2}{\text{g}} \right) = \sum_n m_n \times \frac{\text{surface area of a single particle} \left(\frac{\text{m}^2}{\text{particle}} \right)}{\text{volume} \left(\frac{\text{m}^3}{\text{particle}} \right) \times \text{density} \left(\frac{\text{g}}{\text{m}^3} \right)} \quad (6)$$

The sum is over n histogram bins, where m_n is the percentage of the total number of particles contained in histogram bin n . Geometric surface area was also calculated for the <37 nm> particles, but the BET surface area was used in the rate calculations for that size fraction due to uncertainties in how well the model applies to the particles of differing morphologies. Nevertheless, the two methods (BET and geometric surface areas) agreed in this case to within 3% (see Results section below).

2.4.1. BET surface area

Larger particles were freeze-dried after centrifugation. The powder was degassed overnight at either 150°C or 220°C followed by a 6-point BET isotherm in a Quatachrome Nova 1000 N₂-BET adsorption analyzer. Changing the degassing temperature and mild crushing of the sample in a mortar and pestle followed by reanalysis did not affect the results. Surface areas determined for ultrafine particles (~< 15 nm diameter) are typically lower for BET measurements than those based on geometric models, for example with nanocrystalline GaAs (Hagan et al., 1995), ZnO, and Al₂O₃ (Yao et al., 2001). For this reason, the smallest particles (<7.3 nm> sample) were not subjected to freeze-drying and nitrogen adsorption analysis; the geometric surface area was used in rate calculations. As such, any error in the use of a geometric model for rate calculations would likely under- rather than overestimate the rate.

2.5. Manganese Oxidation Experiments

Batch reactors consisted of 250 mL flasks stirred with a magnetic stir bar. 200 mL of hematite suspension, diluted to the desired suspension density, was equilibrated at the desired pH after adding KNO₃ to obtain an ionic strength of 0.001 M. The pH typically drifted lower overnight and was readjusted the following morning. The pH measurements were made with a Radiometer pHC3006 Ag/AgCl combination electrode, which was stable within 0.02 pH units. Test solutions were observed to be O₂ saturated under equivalent reaction conditions using an Orion dissolved oxygen probe. Mn²⁺ was added by slowly mixing 15 or 20 mL of 100 ppm Mn (from Mn(NO₃)₂) into the flask, giving an approximate initial [Mn]_{TOTAL} of 7 or 9 ppm, respectively. The flasks were covered with aluminum foil to block out light and left at room temperature (20°C) during the course of the experiments, typically between 12 and 24 hours.

2.6. Mn(aq) Analysis

The formaldoxime spectrophotometric method (Morgan and Stumm, 1965; Brewer and Spencer, 1971) was used to determine concentrations of Mn²⁺(aq). Unfortunately, hematite absorbs strongly at the necessary wavelength. For accurate analysis, the particles must be removed from the sample. This is accomplished in this study following a modified procedure from that of (Abel, 1998) as follows: Eight mL of the sample suspension was removed from the reactor and pipetted into each of four 2 mL microcentrifuge tubes. The tubes were centrifuged at 4°C and 14,000-16,000 rcf for 20 minutes. The top supernatant was carefully removed and placed into a 15 mL tube. The volume of the tube was adjusted to 6 mL, and the following reagents were added: 1.2 mL of formaldoxime reagent (stock prepared by dissolving hydroxylamine hydrochloride in MilliQ doubly-distilled water,

adding 37% formaldehyde solution, and making to volume), 3 mL of 5 M NaOH, and MilliQ water for a final volume of 15 mL. Standards of 0.4, 0.5, 1.0, and 3.0 ppm Mn are prepared by dilution from a 1,000 ppm commercial buffered Mn standard. Blanks, standards, and samples are analyzed for absorbance at 450 microns in a Beckman DU 640 spectrophotometer. All standards have a standard error on the order of 2×10^{-5} abs/ppm Mn.

2.7. Data Analysis

Before significant precipitation of manganese oxide and autocatalytic rate control, it is expected that the initial rates will be first order with respect to $[\text{Mn}^{2+}(\text{aq})]$. The reaction proceeds slowly enough that the exponential relationship between $[\text{Mn}]$ and time under pseudo-first order conditions can be approximated by a straight line for a certain initial period. As such, the initial data points should be able to be fit with a linear equation

$$[\text{Mn}^{2+}] = a_1 + b_1 t \quad (7)$$

where a_1 and b_1 are the y-intercept and slope of the line, respectively, and t is time. The derivative $-d[\text{Mn}^{2+}]/dt$ is the slope of the line, or the coefficient b_1 ; thus the value of b_1 gives the uncorrected (for surface area) rate of the reaction at $t=0$ (Rimstidt, 1993).

The rate of reaction determined in these experiments can then be related to the heterogeneous rate constant k_{het} by the relationship given in the following rate law (Diem and Stumm, 1984) (8):

$$\text{rate} = k_{\text{het}} [\text{Mn(II)}]_0 [\text{O}_2] [> \text{SOH}] [\text{OH}^-]^3 \quad (8)$$

where all of the values except k_{het} are known or can be calculated/estimated. $[\text{Mn}]_0$ is the aqueous manganese concentration at the first sampling time; the time corresponding to the initial rate. The value for dissolved oxygen, $[\text{O}_2]$, for the solutions at the appropriate temperature was measured to be $10^{-3.64}$ M. In order to compare results using different particle sizes with equal pH and suspension densities, the measured rate of manganese loss from solution was adjusted to account for the surface area of the particles. The surface area is folded into a term describing the estimated concentration of surface hydroxyl groups $[> \text{SOH}]$; this term requires an assumption about the spatial density of hydroxyl functional groups on the mineral surface.

The concentration of surface sites was assumed to be 6 sites/ nm^2 based on previous measurements of OH/ nm^2 on hematite surfaces include 2.5 OH/ nm^2 for acid titration (Karasyova et al., 1999), 5.5-10 for IR and water adsorption (Yates and Healy, 1975), 22.5 for isotopic exchange (Yates and Healy, 1975), 6 for the (012) face using thermal desorption of adsorbed water (Henderson et al., 1998), and 4.3-9 for whole crystals or individual faces with

crystallographic and computational models (Yates and Healy, 1975; Barron and Torrent, 1996; Venema et al., 1998; Wasserman et al., 1999). The surface site density is combined with the following parameters to yield the estimated concentration of surface hydroxyl functional groups:

$$[>\text{SOH}] \left(\frac{\text{mol}}{\text{L}} \right) = \frac{6 \text{ } >\text{SOH}}{\text{nm}^2} \times \frac{1 \text{ mol}}{6.02 \times 10^{23} \text{ } >\text{SOH}} \times \text{susp. den.} \left(\frac{\text{g}}{\text{L}} \right) \times \text{surf. area} \left(\frac{\text{m}^2}{\text{g}} \right) \times \frac{10^{18} \text{ nm}^2}{\text{m}^2} \quad (9)$$

The suspension density of the syntheses were determined by weighing empty 2 mL tubes, filling the tubes with suspension, evaporating the water in a 90°C oven, and re-weighing the tubes. The final [$>\text{SOH}$] values were used when calculating rates using the rate law of eq. 8.

3. RESULTS

3.1. Hematite Synthesis

The products of nanoparticle synthesis were hematite as determined by electron diffraction; no d-spacings characteristic solely of ferrihydrite were present (Fig. 2). The smaller particles had a platelike morphology and a mean diameter of 7.3 ± 1.9 nm (Fig. 2a), which we refer to as $<7.3 \text{ nm}>$. The full size distribution histogram is shown in Fig. 3a. As measured by AFM, heights of these particles averaged 1.5 nm. The diameter of the particles using AFM is much larger than that measured in the TEM due to tip-sample interaction; however, AFM provides extremely accurate height data. The geometric surface area calculated from the above method for the $<7.3 \text{ nm}>$ sample using TEM diameters and average particle heights determined from AFM measurements is $210 \text{ m}^2/\text{g}$ (compared with the geometric surface area of $230 \text{ m}^2/\text{g}$ by Mulvaney et al., 1988, of 5 nm mean diameter hematite particles). Larger hematite had a mean diameter of 36.7 ± 13.2 nm, but a wide size distribution (Figure 3b), both platelike and rhombohedral morphologies (Figure 2b), and an average thickness of approximately 8 nm. The geometric and BET surface areas of the $<37 \text{ nm}>$ sample were determined to be $40 \text{ m}^2/\text{g}$ and $39 \text{ m}^2/\text{g}$, respectively.

3.2. Manganese Oxidation

The log transformed rate of hematite-promoted manganese oxidation is presented in Figure 4 as a function of pH. Rates have been corrected for the surface area and mass of particles, but no explicit rate law is assumed other than first-order with respect to aqueous Mn^{2+} concentration. Under the assumption of pseudo-first order conditions, rates can only be compared strictly vertically along the y-axis direction. At any given pH over the range of measurements, the difference in rate is approximately one to one and a half orders of magnitude greater for sample <7.3 nm> than sample <37 nm>. Two distinct groupings of rates appear for the <7.3 nm> particles, perhaps related to the ratio of available surface hydroxyl groups to the amount of Mn in the system. The higher assemblage of rates corresponds to the lowest ratio of estimated surface hydroxyls [$>\text{SOH}$] to amount of initially added Mn^{2+} , or equivalently, the highest Mn^{2+} loading on the surface. Loadings ranged from [$>\text{SOH}$]/Mn(ads) of approximately 1 to 8. An additional explanation for the two groupings may be inaccurate response of the pH electrode in the pH 7.2-7.4 range. Various electrodes calibrated with the same buffers responded differently in the suspensions of charged nanoparticles. Each of the lines plotted in Figure 4 have slope $\log \text{rate}/\text{pH} = 3$ (they are not best-fit lines). The slopes of these trend lines suggest a 3rd order dependence of the reaction rate on pH, although there is no *a priori* reason why a complicated reaction on a solid surface should have an integer reaction order (Masel, 2001).

Applying the Diem and Stumm kinetic model (Diem and Stumm, 1984) but assuming a 3rd order pH dependence instead of the suggested 2nd order dependence gives values of the rate constant in $\text{M}^{-4}\text{day}^{-1}$. Log transformed values of the rate constant are plotted vs. pH in Figure 5. Error bars depict the error propagated through the various experimental variables using standard techniques (Garland et al., 2003).

4. DISCUSSION

4.1. Size Quantization Effects in Hematite

Models of electronic structure effects on reactivity as a function of particle size must be carefully considered for each particular system of interest. The term “quantum confinement” does not strictly apply to hematite because electrons are transported in hematite as d-orbital localized Fe^{2+} states (Rosso et al., 2003) related to the correspondingly narrow 3d bands (Catti, 1995). This is in contrast with many other important semiconducting minerals and compounds where the lowest conduction band states are significantly delocalized. On the other hand, size quantization effects are expected to be important in the hematite valence band, where a majority of the states near the Fermi level have O2p character. The covalent Fe-O interactions, especially along [001] and associated with face-sharing octahedra, lead to a fairly broad O2p band. Photoelectron measurements of isostructural corundum suggest an O2p bandwidth of approximately 6-8 eV, or ~600-800 kJ/mol (Kowalczyk et al., 1977; Catlow et al., 1988; Lad and Henrich, 1989). In the <7.3 nm> sample, the height (thickness of particles along [001]) is only ~1.5 nm, well within the size range where electronic structure effects were observed in other oxide nanocrystals (Anpo et al., 1987; Borgohain et al., 2000; Sant and Kamat, 2002; Yanhong et al., 2004). The O2p DOS should change most near the Fermi level.

4.2. Theoretical Explanations for Increase in Rate Based on Electron Transfer Theory

Electron transfer theory provides a framework for rationalizing the relationship between nanomineral size/properties and reaction rate. For detailed discussions of electron transfer theory, see for example Marcus and Sutin (1985), Miller et al. (1995), Rosso and Rustad (2000),

and Rosso and Morgan (2002). The rate constant for a nonadiabatic (see below) electron transfer reaction (disregarding quantum effects such as tunneling) can be given by

$$k_{et} = \frac{2\pi}{\hbar} \langle V_{AB} \rangle^2 \frac{e^{-(\Delta G^{\circ'} + \lambda)^2 / 4\lambda RT}}{\sqrt{4\pi\lambda RT}} \quad (10)$$

where \hbar is 2π divided by Plank's constant, $\langle V_{AB} \rangle$ is the electronic coupling matrix element describing the energy lowering due to the coupling between the initial and final states of the electron transfer, $\Delta G^{\circ'}$ is the free energy of reaction corrected for the electrostatic work required to bring the reactants together, and λ is the reorganization energy of “inner sphere” coordinated vibrational modes and “outer sphere” solvent molecules between initial and final states. Nonadiabatic electron transfers are best described by a system of two localized electronic states, initial (ψ_A) and final (ψ_B). The splitting between the two potential surfaces $\psi_A(q_i)$ and $\psi_B(q_j)$ at the transition state configuration is given by $2V_{AB}$, where $q_{i,j}$ are coordinates parameterized by the normal modes of $\psi_A(q_i)$ and $\psi_B(q_j)$ (see Fig. 6 for a pictorial representation of these quantities). Note that the activation energy ΔG^*_{non} (again, corrected for electrostatic work to bring reactants together) is related to both the corrected free energy of reaction $\Delta G^{\circ'}$ and the reorganization energy λ as given by eq. 10. Also note that due to the Franck-Condon principle, in the classical limit radiationless electron transfers can only occur at the transition state geometry, as momentum cannot be transferred between electrons and nuclei.

The free energy of the manganese oxidation reaction, $\Delta G^{\circ'}$, would be expected to change as a function of hematite nanoparticle size. It has been demonstrated that the redox potential of adsorbed metal ions is lower than that of equivalent aqueous ions (Stumm, 1992), which has been shown to accelerate their rate of oxygenation (Wehrli et al., 1989) similar to hydrolysis (Rosso and Morgan, 2002). Fig. 7a illustrates the change in the standard state redox potential of the aqueous $Mn^{2+}(OH_2)_{6-x}(OH^-)_x / O_2$ redox couple for x (the number of OH^- ligands bonded to

the metal) equal to 0-2 from quantum calculations (Rosso and Morgan, 2002). The reactivity trends indicate that the electron density donating properties of the ligand(s) control the value of the “effective” redox potential for the ion. This has also been shown clearly with both the $\text{Mn}^{2+/3+}$ and $\text{Mn}^{3+/4+}$ systems, where a linear relationship was found between the electron donating properties of a series of structurally similar ligand complexes and the redox potential of the coordinated Mn ion (Lewis et al., 2001). The data of Lewis et al. (2001) are presented in Fig. 7b. These results express the redox potential of $\text{Mn}^{3+/2+}$ *cis,cis*-1,3,5-triaminocyclohexane complexes as a function of the electron donating/withdrawing power of substituents. The electron density donating/withdrawing power is quantified by a number known as the Hammett parameter, where higher numbers indicate increasing electron withdrawing power. Their data (Fig. 7b.) demonstrates that as the electron withdrawing power of the ligands increase, the redox potential of the coordinated Mn also increases. In regards to the Mn^{2+} oxidation experiments, this implies that as the electronic structure of the hematite becomes more quantized, the increased Lewis basicity of the surface oxygens (Noguera et al., 2002) decreases the redox potential of the adsorbed Mn (ie., makes the reaction more energetically favorable). The increase in Lewis base strength of the hematite oxygen atoms is related to the electronic coupling matrix element ($\langle V_{AB} \rangle$ in eq. 10), both increasing the preexponential $\langle V_{AB} \rangle^2$ term and decreasing the height of the activation barrier (the splitting between the diabatic and adiabatic energy surfaces (Rosso and Rustad, 2000)). In addition, molecular dynamics calculations of proton surface charging on 3-8 nm goethite particles indicate that certain crystallographic terminations of faces lead to edges with oxygen atoms that have increased Lewis base character (Rustad, in press).

Any changes in the geometry of Mn^{2+} sorptive complexes as a function of size would be expected to change the reorganization energy (λ in eq. 10) of electron transfers involving the Mn ion. One of the barriers to electron transfer reactions involving Mn^{2+} is the high reorganization energy involved with the changes in bond lengths around the nearly octahedral Mn^{2+} d^5 coordination sphere and the highly distorted Mn^{3+} d^4 coordinative environment (Macartney and Sutin, 1985). Adsorbing at or diffusing to defect, edge, or other environments that disrupt the Mn^{2+} coordination geometry should increase the rate as a result of the decrease in the inner sphere reorganization energy. Decreasing the reorganization energy λ both decreases the distance between the equilibrium bond length and the vibrational coordinates required to reach the transition state geometry on the potential surface and decreases the height of the activation barrier. Also, $\langle V_{AB} \rangle$ is very sensitive to the precise geometry of the system, as in general electron transfer rates are exponentially related to distance (Marcus and Sutin, 1985). This has been observed on hematite surfaces, where the reaction was shown to initiate at the base of steps (Junta and Hochella, 1994). At step bases, the Mn^{2+} coordination complex loses a degree of freedom as compared with binding on terraces. The increase in coordinatively undersaturated or distorted surface atoms as the size of hematite nanoparticles is reduced (Chen et al., 2002) also provides sites for rate enhancement, which may reflect the greater percentage of edge vs. face sites. Investigations of Pb^{2+} binding on hematite surfaces have shown that the binding mechanism is different on particle edges and faces (Bargar et al., 2004).

4.3. Validity of Kinetic Model – Macroscopic vs. Microscopic

Although these data suggest a dramatic increase in heterogeneous manganese oxidation rate as the particle size decreases below 10 nm, complicating factors must be considered in

interpreting the data. One consideration is the accuracy of the rate law as a model for reactions in this system. The rate laws for Mn oxidation were initially derived empirically for a small set of reaction conditions (Morgan, 1967), later modified by adding a surface complexation model to account for the pH-dependent adsorption behavior of Mn^{2+} (Davies and Morgan, 1989). Observations such as a reaction order of 1.6 vs. pH in experiments with goethite (Davies and Morgan, 1989) and the approximately third order $\log k_{\text{het}}$ vs. pH trend in this study suggest the pH dependent behavior of heterogeneous manganese oxidation reaction cannot be completely captured in simple second order dependence such as that suggested by the experiments of Diem and Stumm (1984). This is further demonstrated by microscopic observations demonstrating the heterogeneity of surface reactivity as manganese oxidation proceeds at step sites on hematite (001) surfaces and precipitates in isolated clusters (Junta and Hochella, 1994). Regardless of the accuracy of the conceptual and mathematical model describing the process, previous kinetic studies have shown that the heterogeneous oxidation of $\text{Mn}^{2+}(\text{aq})$ is first order with respect to $[\text{Mn}^{2+}(\text{aq})]$ (Kessick, 1975; Sung and Morgan, 1980; Hem, 1981; Diem and Stumm, 1984; Davies and Morgan, 1989). Analysis with this assumption only (ie., Fig. 4) and also assuming additional information about the form of the rate law (ie., Fig. 5) both result in the same conclusions about the relative rates of manganese oxidation between the two particle sizes. Ideally, direct observations of the system during reaction would lead to a rate law that matched with the microscopic mechanisms (Junta-Rosso et al., 1997). This has not been accomplished in our case due to the extreme smallness of the reactant particles.

Equation (1) is clearly an overall reaction; a composite of several elementary steps. The electron transfer between the adsorbed Mn and dissolved O_2 is considered to be the rate-limiting step (Luther, 1990; Rosso et al., 2003). The adsorbed Mn^{3+} eventually becomes incorporated

into a growing manganese oxide precipitate as the reaction proceeds by the autocatalytic mechanism, and superoxide radicals are presumably formed from O_2 as suggested in the typical Haber-Weiss interpretation of the reaction mechanism (Rosso and Morgan, 2002). Oxygen isotope labeling experiments indicate that some of the oxygen in heterogeneously precipitated Mn-oxide minerals is derived from O_2 (Mandernack et al., 1995). The reaction (1) as written suggests the stoichiometry of 2 electrons transferred from Mn^{2+} for each O_2 reduced. Four electrons are required to achieve the full reduction of oxygen to water. The mechanistic role of the produced superoxide, hydrogen peroxide, and other reactive intermediates has not been explored to the knowledge of the authors.

An additional complicating factor to rate interpretation involves the particle morphologies. A significant proportion ($\sim 1/3$) of the $<37\text{ nm}>$ sample have rhombohedral morphologies, exposing crystal faces that presumably have different reactivities. The smaller particles have platelike morphology only. This cannot explain the rate differences. If the rhombohedral particles are more efficient at promoting the Mn oxidation reaction, the larger particles should coincide with faster rates; this is not the case. If they were significantly less efficient, the larger platelets that constitute $2/3$ of the $<37\text{ nm}>$ sample would control the rate. Consider an “end-member” scenario in which the rhombohedral particles do not contribute to the Mn oxidation rate (ie., they promote the reaction appreciably less than the platelike particles, such that their contribution to the rate is insignificant). In this situation the measured rate would be dominated by the surface area contributed from the platelets, reducing the “reactive” surface area of the $<37\text{ nm}>$ sample as a whole by $1/3$. Even in this extreme scenario, the decreased reactive surface area can only account for an increase in $\log k_{\text{het}}$ for the $<37\text{ nm}>$ sample by

about 0.2 (from an average of $25.95 \text{ M}^{-4} \text{ m}^{-2} \text{ day}^{-1}$ to $26.13 \text{ M}^{-4} \text{ m}^{-2} \text{ day}^{-1}$ for analysis as in Fig. 5), not nearly enough to “explain” the difference in reactivity as a function of particle size.

5. SUMMARY AND IMPLICATIONS

As the size of hematite particles approach the nanometer size regime they become more efficient at promoting the oxidation of $\text{Mn}^{2+}(\text{aq})$ in the presence of $\text{O}_2(\text{aq})$. Reactivity differences as a function of size is likely related to the changing electronic and geometric structure of the hematite surfaces. Although the details of these property changes are specific to the system of interest, changing electronic and geometric structure changes are likely to be general phenomena related to the transition between bulk and molecular scale materials and the extreme surface area/volume ratio. Further experimental investigations with various mineral and aqueous systems can be combined with observations of natural systems to begin to elucidate the significance of increased reactivity of nanoparticulate minerals. For example, TEM observations of associations between nanoscale iron and manganese (hydr)oxide minerals in a river floodplain affected by mining activities and acid mine drainage suggest heterogeneous Mn^{2+} oxidation was responsible for a least a portion of the Mn mineralization (Hochella, in press a). These Fe and especially Mn oxide minerals are responsible for significant heavy metal uptake.

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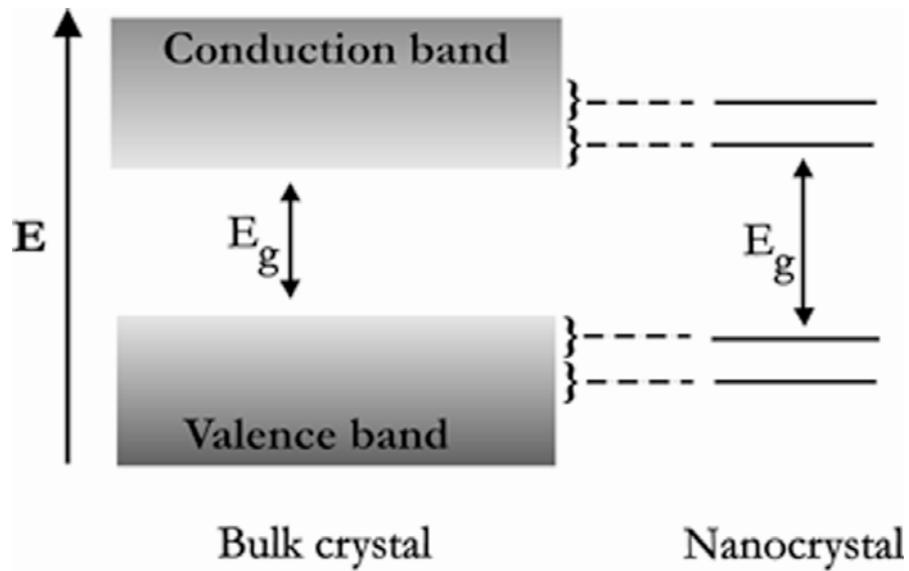


Fig. 1. Schematic of allowed electron energy states in bulk vs. nanocrystalline semiconductors near the top of the valence band demonstrating the band gap widening.

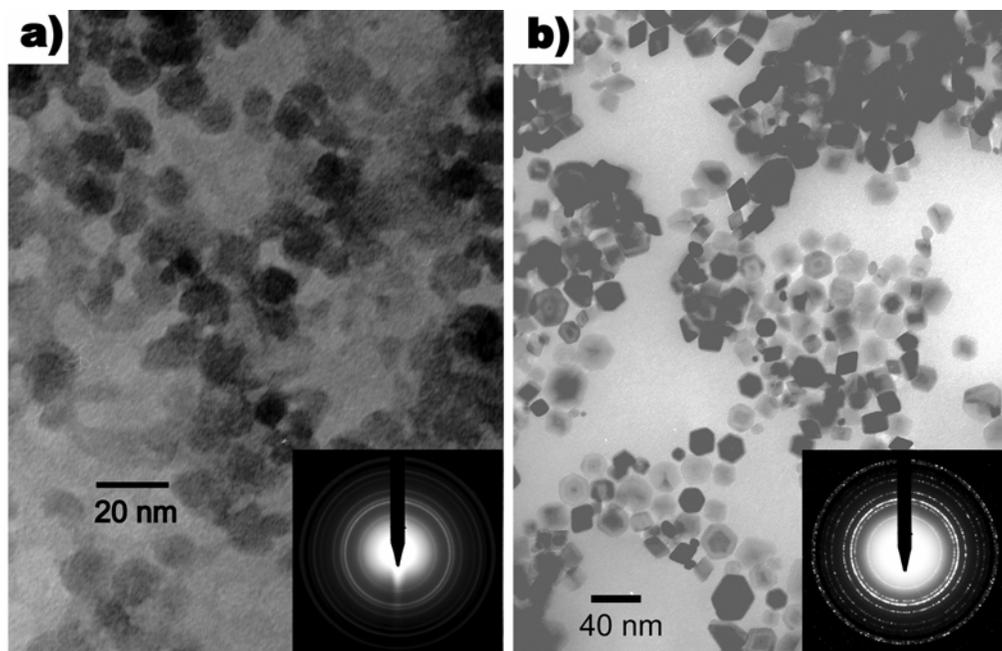


Fig. 2. TEM image of hematite nanoparticles with a) 7.3 nm and b) 37 nm average diameter.

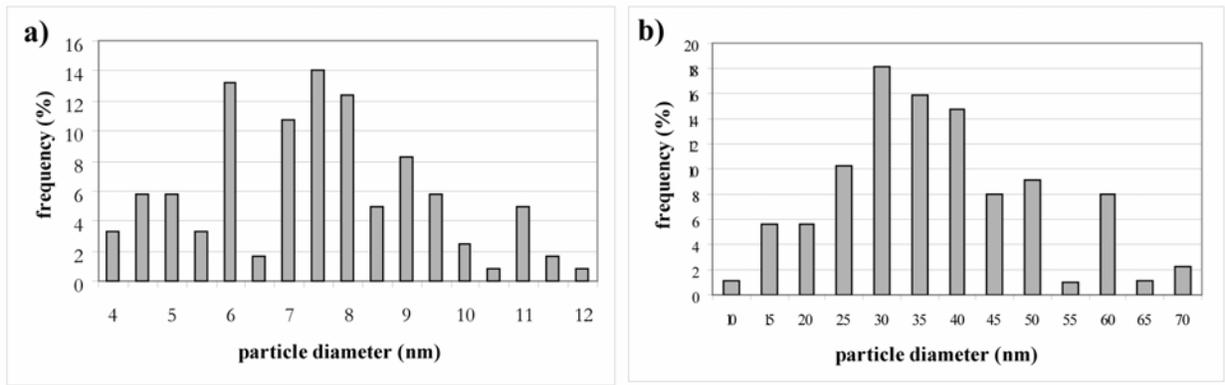


Fig. 3. Histograms of a) <7.3 nm > and b) <37 nm> hematite nanoparticle size distributions.

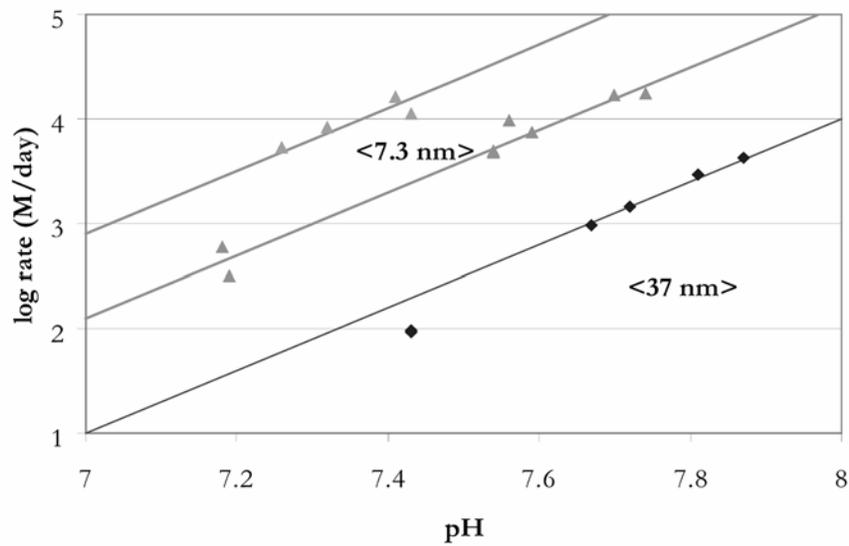


Fig. 4. Log rate vs. pH. Lines each have a slope of 3. Rates for the <7.3> nm particles fall into two groupings. See text for details.

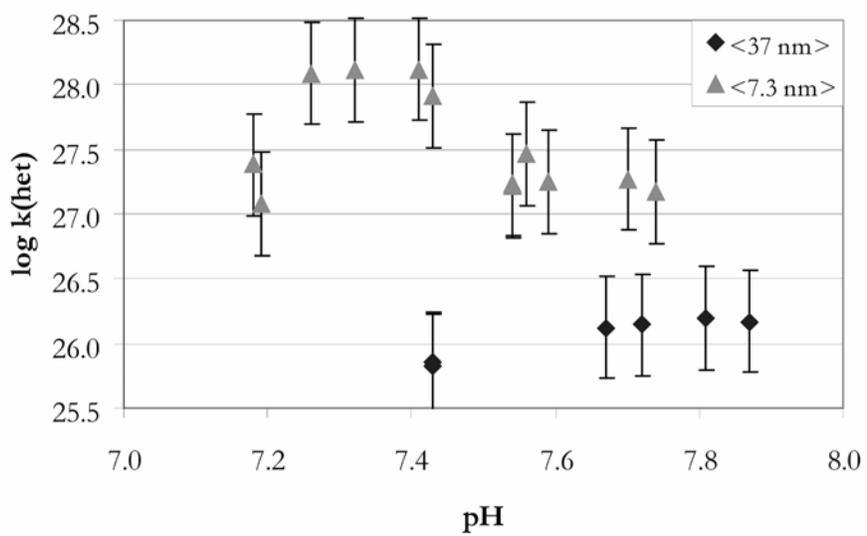


Fig. 5. Log heterogeneous Mn oxidation rate constants determined from this study, assuming semiempirical rate law (eq. 7).

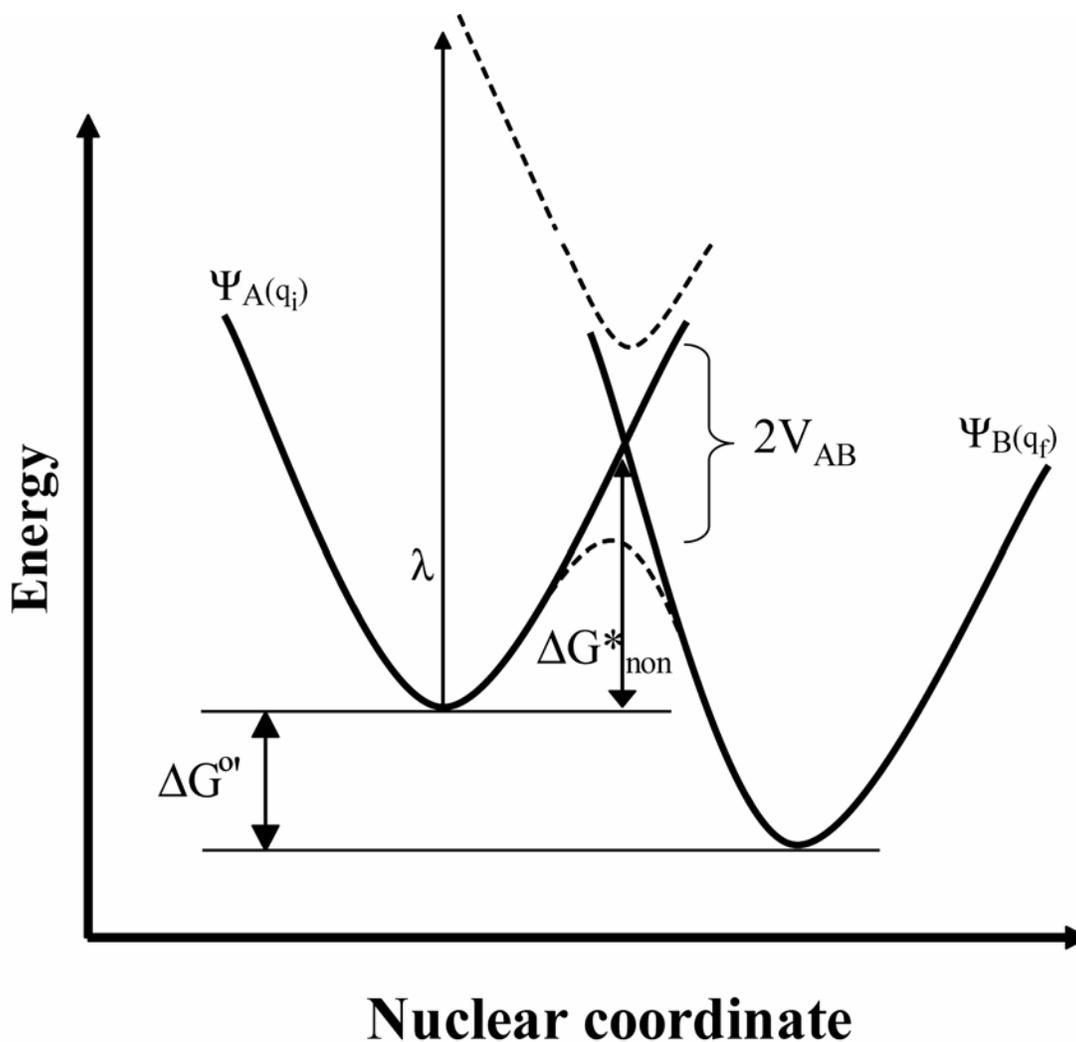


Fig. 6. Schematic of a potential energy surface as a function of the normal mode nuclear coordinates corresponding to the reaction coordinate. Energy and free energy are used synonymously as the entropy of reaction is considered to be negligible. The solid curves represent the nonadiabatic initial and final states. The dotted curves represent the adiabatic potential energy surfaces, where the electron is delocalized between the initial and final states. The splitting between the two cases, $2V_{AB}$, is a function of the electronic coupling between the initial and final states. Increased coupling causes the reaction to become increasingly adiabatic and lowers the potential energy barrier. After Rosso and Morgan (2002).

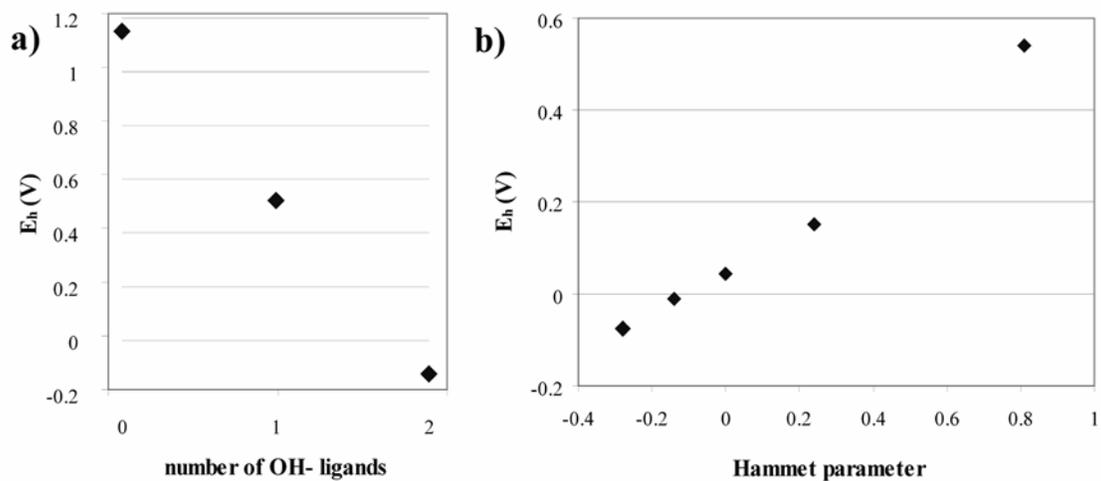
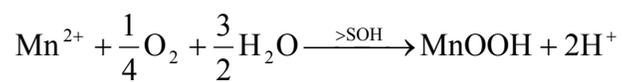


Fig. 7. a) Redox potential of Mn^{2+}/O_2 couple as a function of the number of coordinated OH ligands as calculated by ab initio methods; data from Rosso and Morgan (2002). b) Redox potential of the central $Mn^{2+/3+}$ ion of *cis,cis*-1,3,5-triaminocyclohexane complexes as a function of the electron donating/withdrawing power of substituents, as given by the substituents' Hammett parameter. Examples of substituents are methoxy (Hammett parameter = -0.28) and nitro (Hammett parameter = +0.81) groups. Increasing Hammett parameters correspond to an increase of the ligand's ability to withdraw electron density from the Mn ion. Data are from Lewis et al. (2001).

ERRATA

Equation (1) should be replaced by:



with the correct reference of Diem and Stumm (1984).

Chapter 3

Insights for size-dependent reactivity of hematite nanomineral surfaces through Cu²⁺ sorption

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ABSTRACT

Sorption edges for Cu^{2+} were measured on hematite nanoparticles with average diameters of 7 nm, 25 nm and 88 nm in 0.1 M NaNO_3 . The pH edges for the 7 nm hematite were shifted approximately 0.8 pH units lower than that for the 25 nm and 88 nm samples, demonstrating an affinity sequence of 7 nm > 25 nm = 88 nm. Although zeta potential data suggest increased proton accumulation at the 7 nm hematite surfaces, changes in surface structure are most likely responsible for the preference of Cu^{2+} for the smallest particles. As Cu^{2+} preferentially binds to sites which accommodate the Jahn-Teller distortion of its coordination to oxygen, this indicates the relative importance of distorted binding environments on the 7 nm hematite relative to the 25 nm and 88 nm particles. This work highlights the uniqueness of surface reactivity for crystalline iron oxide particles with diameters less than approximately 10 nm.

1. INTRODUCTION

Nanoscale (hydr)oxide minerals, those having physical dimensions of approximately 1-50 nm, are common constituents of the natural world (BIGHAM et al., 2002). Over this length scale, materials have properties that are dependent on the particle size (HOCELLA, 2002). In particular, the relationships between iron oxide mineral sizes and their properties as related to geochemical reactivity are just beginning to be explored. Iron oxides are involved in a great variety of geochemical processes, such as sorption of metals, serving as a terminal electron acceptor for microbial respiration, participation in photochemical reduction, etc. Nanoscale iron oxide particles with surface-bound metals are found many kilometers downstream from mining sites, suggesting they may be susceptible to colloid-mediated transport of sorbed contaminants (HOCELLA et al., 2005a; HOCELLA et al., 2005b). Any and all of these processes are likely to show size-dependent reactivity on crystalline iron oxide nanoparticles, such that each process will occur with different thermochemical and kinetic relationships as a function of size. For example, Mn^{2+} oxidation rates on 7 nm average diameter hematite particles were shown to be up to two orders of magnitude faster than those on with average diameter 37 nm, even when normalized to surface area (MADDEN and HOCELLA, 2005). Based on arguments from electron transfer theory, it was hypothesized that the rate differences may be related to changes in the coordination environment for Mn^{2+} adsorbed on the different sizes of hematite, specifically a decrease in symmetry of the coordination complex. The decrease in symmetry was hypothesized to stabilize Mn^{3+} ($3d^4$ electron configuration) relative to Mn^{2+} ($3d^5$ electron configuration).

Other concurrent work on iron oxide nanoparticles has demonstrated a change in the distribution of binding environments as a function of size. Kim et al. (in preparation) studied the sorption of trace and heavy metals on goethite-like iron oxide nanoparticles with X-ray absorption fine structure (EXAFS). The simplest explanation to describe the changes in metal-Fe bond distances observed in the EXAFS spectra is that there is a decrease in the symmetry of bonding environments on the smallest particles relative to the larger particles. In addition, using molecular dynamics simulations Rustad and Felmy (2005) found that certain edges of 2-8 nm goethite nanoparticles give rise to potential binding sites with longer Fe-O_{water} bond lengths and thus increased Lewis base character. These edge sites would be most susceptible to electron transfer reactions.

Mineral surface defects, topographic features, and step/particle edges are known to control many aspects of reactivity at the mineral-water interface, yet it remains challenging to directly probe their atomic and electronic structure in solution (HOCELLA, 1990; BROWN and PARKS, 2001). Some progress has been made with aqueous phase tunneling microscopy (e.g., EGGLESTON et al., 2003) and theoretical modeling (e.g., BECKER et al., 1996). Undercoordinated surface metal atoms and related oxygen vacancies are clearly key to many aspects of industrial catalysis of gas-phase molecules on transition metal oxides (KIM et al., 1979; HENRICH and COX, 1996; SADYKOV, 2000). Undercoordinated surface atoms are known to exist in greater proportion on oxide nanoparticles in vacuum as the particle size decreases (CHEN et al., 1997; CHEN et al., 2002; RAJH et al., 2002; ZHANG et al., 2003; FERNANDEZ-GARCIA et al., 2004).

Studies on model materials such as MgO (STIRNMAN et al., 1996; LIU et al., 1998a; CHIESA et al., 2005) and more geochemically relevant materials (BECKER et al.,

1996; HENDERSON et al., 1998; ROSSO et al., 2000; BECKER and ROSSO, 2001; ROSSO, 2001; BORDA et al., 2003; ELSETINOW et al., 2003) have begun to provide fundamental information on the role that defects and undercoordinated surface metal atoms play in the chemical reactivity of surfaces. Certainly hematite surfaces are known to have heterogeneous surfaces, including topographic features and defects, such that only certain portions of the surface will be reactive to any given geochemical process (JUNTA-ROSSO and HOCELLA, 1996; JUNTA-ROSSO et al., 1997; LIU et al., 1998b; SAMSON and EGGLESTON, 1998; WANG et al., 1998; SAMSON and EGGLESTON, 2000; EGGLESTON et al., 2003; EGGLESTON et al., 2004; TRAINOR et al., 2004). As the dimensions of the particles approach the nanometer scale, an increasingly large proportion of the surface would be expected to deviate from a flat terrace. Due to the unique arrangements of surface atoms at edges, steps, and other surface defects, metal binding coordination at these sites will be influenced by the local atomic structure, electronic structure, and dielectric field.

In this study, Cu^{2+} ions are used to probe the nature of binding sites on hematite nanoparticles. Cu^{2+} serves as an excellent probe for distorted binding environments. With a $3d^9$ electron configuration, it experiences Jahn-Teller distortion in octahedral coordination, similar to Mn^{3+} , as evidenced both in solution (BAES and MESMER, 1986) and on mineral surfaces (MCBRIDE, 1989; SCHEINOST et al., 2001; PEACOCK and SHERMAN, 2004). Although Cu^{2+} binds strongly to oxide surfaces, it also fractionates strongly to distorted binding sites that are common in natural organic matter (MCBRIDE, 1981; BUERGE-WEIRICH et al., 2002). If the smallest hematite nanoparticles have more distorted binding sites for Cu^{2+} per m^2 of mineral surface area, we would expect to

measure a shift in the pH-dependent sorption behavior of Cu^{2+} which is dependent on particle size.

In addition to its use as a surface probe species, it is also important to keep in mind that the sorption of Cu on oxide surfaces is an important control of Cu distribution in the environment along with complexation to organic matter (JAMES and BARROW, 1981; MCBRIDE, 1981; KABATA-PENDIAS and PENDIAS, 1992). Although Cu is an essential micronutrient, it is toxic at relatively low concentrations. For heavy metals, the copper toxicity threshold for algae, flowering plants, fungi, and phytoplankton is only surpassed by Hg and sometimes Ag (SPOSITO, 1989). Cu has been documented to be associated with nanoscale iron oxide surfaces in relation to mining activities (HOCELLA et al., 1999; HOCELLA et al., 2005b).

2. MATERIALS AND METHODS

2.1 Particle synthesis and characterization

2.1.1. Hematite synthesis

Two synthetic hematite samples were prepared in our laboratory, somewhat following the instructions from method 1 and method 4 of Schwertmann (2000). For synthesizing larger hematite particles (method 1), a flask containing 500 mL of 0.002 M HCl was brought almost to a boil on a heat plate. 4.04 g of $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ was added and the bottle was vigorously shaken. Immediately, the bottle was returned to the heat and held at a very mild boil for 7 days, periodically replacing evaporated water.

The smaller hematite nanoparticles were synthesized (method 4, (SCHWERTMANN, 2000)) by slowly dripping 60 mL of 1 M ferric nitrate solution from a burette into 750

mL water boiling on a heat plate. After the drip solution was consumed, the nanoparticle suspension was removed from heat.

Dialysis tubing was rinsed several times in water baths at least one day before adding sample. Cooled suspensions were dialyzed against MilliQ water until the conductivity of the dialysis water nearly reached that of pure MilliQ. For the smallest particles (method 4), a final dialysis was performed against pH 4 MilliQ water, adjusted with HNO₃.

An additional synthetic commercial sample was also used. Anhydrous ferric oxide (Fisher Scientific) was used without further treatment. Lot impurity information listed the following: As 0.002%, Nitrate 0.01%, Phosphate 0.005%, Sulfate 0.07%, Mn 0.02%, Cu 0.002%, Zn 0.008%, substances not precipitated by NH₄OH 0.08%.

2.1.2. Characterization

Transmission Electron Microscopy (TEM) was used to determine the shape and diameter of the particles. Mineral suspensions were dropped onto formvar/carbon coated Cu grids and allowed to dry. Dried grids were imaged in a Phillips EM 420T TEM. Negatives of images and diffraction patterns were scanned for subsequent image analysis.

The height dimension of the particles was measured with Atomic Force Microscopy (AFM). Dilute mineral suspensions were dropped onto Si wafer chips and heated briefly at 60°C in an oven. The remaining suspension was blotted with a kimwipe. Images were collected in contact mode with oxide-sharpened SiN tips. Images were flattened (with exclusion of particle areas) before height analysis.

Surface area for the smallest particles was determined geometrically using 2-D measurements from TEM negatives and height measurements by AFM (MADDEN and HOCELLA, 2005). Briefly, a size distribution was generated in 1 nm histogram bins. The particles were assumed to be irregular hexagonal plates (both length and width measured in TEM negatives), and the surface area was calculated for a particle in each histogram bin. The total surface area is obtained by multiplying the surface area of an average particle from each bin by the fraction of the total particles represented by that bin. Surface area of the commercial sample was measured with a 6-point BET N₂ isotherm after degassing for 24 hours at 80°C.

Powder X-Ray Diffraction (XRD) was performed using a Scintag powder X-ray diffractometer using Cu radiation and a step size of 0.02 degrees 2 θ .

For determination of the particle surface potential, mineral suspensions (0.5 g/L) were prepared with 0.01 M NaCl in tubes individually adjusted to various pH values. Zeta potential measurements were conducted in a Malvern Zetasizer HS 2000 with a cell potential of 200 mV.

2.2 Batch sorption experiments

Batch sorption experiments were performed in a Teflon beaker contained within a custom-designed glass reaction vessel. N₂ gas was passed through O₂ and CO₂ traps before bubbling into the reactor. A floating Teflon magnetic stir bar provided agitation. Positive pressure, necessary for CO₂ exclusion, was observed by using a gas outlet port leading to a water-filled beaker. A Radiometer pH3006 Ag/AgCl combination electrode provided pH measurement. Cu was added as CuCl₂·2H₂O. Solutions used to

adjust pH were 0.1 M HNO₃, 0.1 M NaOH, and 0.001 M NaOH. Reactions occurred at room temperature, measured to be 20.5-21.5°C. Samples were extracted and centrifuged at forces up to 140,000 rcf for 15 min before preservation in HCl. Metal concentrations were measured by ICP-AES. NaNO₃ (0.1 M) was chosen as the electrolyte. Copper sorption has been shown to have ionic strength dependencies (ROSE and BIANCHI-MOSQUERA, 1993), as has been measured for Cu on quartz (CRISCENTI and SVERJENSKY, 1999). No ionic strength dependence has been observed for Cu sorption on iron oxides in nitrate electrolytes (SWALLOW et al., 1980; JUNG et al., 1998).

3. RESULTS AND DISCUSSION

3.1. Particle characteristics

Average diameters for the particles are 7 nm, 25 nm (synthetic samples), and 88 nm (Fisherbrand sample). The shapes of the two synthetic samples are pseudo-hexagonal, as observed by TEM (Fig. 1a,b), while the commercial sample is more irregular (Fig. 1c). Diffraction patterns of 7 nm and 25 nm samples have only d-spacings characteristic of hematite (Fig. 2), while the Fisher sample pattern is characteristic of hematite with maghemite (γ -Fe₂O₃) and siderite (FeCO₃) present as minor impurities, based on the observed additional d-spacings of 2.99, 2.79, 2.04, 1.77, and 1.65 Å. The XRD pattern for the 7 nm and 25 nm samples exhibit peak broadening, an expected phenomenon (WAYCHUNAS, 2001). Surface areas were calculated for the in-house synthetic samples as 188 m²/g and 62 m²/g for the 7 nm and 25 nm hematite, respectively. Surface area for the 88 nm particles was measured to be 9.1 m²/g.

3.2. Cu sorption

Sorption edges of Cu^{2+} on hematite nanoparticles are shown as percent Cu sorbed/ m^2 , normalized to the highest sorption value (Fig. 3). The data in Fig. 3 represent surface loadings of $10^{-6.01}$ mol Cu / m^2 and $10^{-6.25}$ mol Cu / m^2 for the 7 nm and 25 nm hematite edges. Additionally, pH edges are presented corresponding to higher Cu^{2+} loadings of $10^{-5.68}$ mol Cu / m^2 on the 25 nm particles and $10^{-5.42}$ mol Cu / m^2 on the 88 nm particles (data summarized in electronic annex EA-1). The edges for Cu^{2+} sorption on the 7 nm average samples contain data points which diverge from their expected values based on sorption edges measured in other studies (e.g., CHRISTL and KRETZSCHMAR, 1999; PEACOCK and SHERMAN, 2004). In most cases, this can be attributed to incomplete removal of nanoparticles during centrifugation.

All samples analyzed for Cu were also analyzed for Fe. The presence of Fe is evidence that some particles were retained in the supernatant after centrifugation or resuspended during supernatant removal. As the pH increases through the edge, these extra particles will have bound Cu that will influence the data in Fig 3. Sorption data was corrected for the amount of Fe-bound Cu by converting the mass of Fe (mg/kg) into a surface area (m^2/L) using a hypothetical particle with the diameter as a fitting parameter. This was done to test the possibility that those particles remaining in the supernatant were significantly smaller than the average particle size. Corrected data, presented in Fig. 4, reflect an average particle size of 7.27 nm (particle mass $3.31 \cdot 10^{-16}$ mg) used in the calculations.

The trends clearly indicate a preference in Cu^{2+} binding in the order 7 nm > 25 nm = Fisherbrand (88 nm average diameter). The positions of the edges, as measured at 50 % of maximum sorption, are qualitatively consistent with other studies of Cu^{2+} sorption

on hematite, although clearly the experimental conditions in each design are reflected in the observed edge positions (CHRISTL and KRETZSCHMAR, 1999; PEACOCK and SHERMAN, 2004).

Despite tendencies to hydrolyze, dimerize, and form surface precipitates (BAES and MESMER, 1986; PALMQVIST et al., 1997; KARTHIKEYAN et al., 1999), sorption behavior on iron oxides at low to neutral pH, low surface loadings, and low total copper is thought to be adequately described by adsorption alone (KARTHIKEYAN and ELLIOT, 1999). Adsorption of Cu^{2+} on iron and aluminum oxides occurs instantaneously relative to the timescale of a sorption experiment; however, diffusion along surfaces and into particle aggregates extends the time required to achieve equilibrium (SWALLOW et al., 1980; PADMANABHAM, 1983; GROSSL et al., 1994; SCHEINOST et al., 2001; SUBRAMANIAM and YIACOUMI, 2001). Equilibration time for each sample in these experiments was 50+/-5 minutes. If diffusion limitation was responsible for causing the differences observed in Cu sorption between the particle sizes, the trend should be opposite - not as much Cu would be sorbed on the smaller particles. Other possible rationalizations such as differences in ionic strength, temperature, surface loading, and total metal added also do not account for the observed trends.

3.3. Zeta potential

Zeta potential results for the hematite samples (0.5 g/L in 0.1 M NaCl) are shown in Fig 5. The point of zero charge (pzc) is the same within error of the measurements, approximately 8.8. Although there has historically been a very large range in measured values for hematite, for the last 20 years they typically fall in the range of 8.5-9.5, compared with 7.8-7.9 for ferrihydrite (CORNELL and SCHWERTMANN, 1996). The 7 nm

particles have a higher absolute value of surface potential at any given pH than the 25 nm particles. One possible explanation is the presence of lower-coordinated surface Fe ions. The surface charge of maghemite, the oxidized form of magnetite, is higher than that of hematite (WATANABE, 1986). It follows that one possible explanation for the increased surface potential of the 7 nm particles is the presence of undercoordinated iron ions, such as those found in maghemite. The hexagonally close-packed oxygen sublattice of hematite can serve as a template for cubic-close packed magnetite/maghemite domains (CONDON, 1998). Multiple surface terminations in domain-like patches have been commonly observed with tunneling microscopy (WANG, 1998; EGGLESTON, 1999; SHAIKHUTDINOV and WEISS, 1999; EGGLESTON et al., 2003). The pzc of maghemite has been measured to be 6.6 (GARCELL et al., 1998) and 6.2 (JARLBRING et al., 2005) due to the higher acidity of certain surface hydroxyl groups relative to those on hematite (WATANABE and SETO, 1993). If maghemite-like domains were present in large amounts on the hematite nanoparticle surfaces, it might be expected that the pzc would shift to a lower value.

The lack of a pzc shift between 7 and 25 nm hematites suggests another mechanism may be responsible for differential surface charging. One such hypothesis is that some acute intersections of faces can lead to a higher dielectric field near the edges. Based on molecular modeling of 2-8 nm goethite particles, protons tend to accumulate in these regions. It was suggested that experimentally this effect would be observed as an increase in proton uptake without a large effect on the pzc, which is consistent with the observed zeta potential data (RUSTAD and FELMY, 2005). Other explanations for the observed zeta potentials include subtle differences in the solution ionic strength or the

presence of surface contaminants. Survey scans done with X-ray photoelectron spectroscopy did not reveal the presence of any contaminants other than adventitious carbon.

3.4. Changes in pH dependent Cu²⁺ binding as a function of size

The pH-dependent adsorption of metal ions on mineral surfaces is controlled by the properties of the ion, the solution, and the surface. The energetics of adsorption can be described as

$$\Delta G_{tot}^{\circ} = \Delta G_{chem}^{\circ} + \Delta G_{coul}^{\circ} \quad (1)$$

in order to separate out the effects of chemical bonding at the surface versus the work done to bring the ion through the potential gradient at the surface (SCHINDLER and STUMM, 1987; STUMM, 1996; SPARKS, 2003). Observed changes in metal binding as a function of hematite nanoparticle size are likely a result of changes to both components.

The results of the Cu sorption experiments do not support the dominance of electrostatic/coulombic interactions. Although the 7 nm particles have a higher positive surface charge below the pzc, they have a greater affinity for Cu²⁺ ions. This supports the dominance of local chemical and surface structural controls in Cu²⁺ adsorption on hematite nanoparticles. However, size-dependent changes in the electrostatic contribution to the adsorption energy, ΔG_{coul}° , are also likely.

The zeta potential data (Fig. 5) show that the potential field at the plane of shear is higher for the 7 nm hematite than the 25 nm hematite particles. The electrical potential can be related to the distribution of diffuse ions, not specifically adsorbed or associated with surface functional groups, by a version of the Boltzmann equation

$$c_{i,x} = c_{i,\infty} \exp\left(\frac{-z_i F \Psi_x}{RT}\right) \quad (2)$$

where $c_{i,x}$ is the concentration of species i at a distance x from the surface, $c_{i,\infty}$ is the concentration of species i in the bulk solution (not influenced by the potential field of the surface), z_i is the charge of species i , F is Faraday's constant, Ψ_x is the potential at a distance x from the plane, R is the gas constant, and T is temperature (PARKS, 1990). Although this Gouy-Chapman model is only appropriate for low potentials, does not account for ion sizes, and assumes an infinitely flat plate (SPOSITO, 1984), a qualitative analysis is possible. Inserting the values $c_{i,\infty} = 0.1 \text{ M NO}_3$ and $z_i = -1$, along with the zeta potentials measured nearest to pH 5 into equation 2 provides a picture of the distribution of nitrate ions between the plane of shear and bulk solution (Fig. 6a) and the corresponding potential distribution (Fig. 6b).

These plots show that, using the Gouy-Chapman model with the plane of shear as the origin of the potential, the potential difference measured between the two particle sizes is enough to cause an increase of nitrate ions at the shear plane of about 35% near the 7 nm particles relative to the 25 nm particles. Similarly, the increase in positive potential would be expected to exclude additional Cu^{2+} ions from the diffuse layer – clearly not supported by the experimental data. Additionally, no ionic strength dependence has typically been found for Cu sorption in nitrate electrolyte (SWALLOW et al., 1980; JUNG et al., 1998; CRISCENTI and SVERJENSKY, 1999).

In addition, it has been suggested that ion binding on mineral surfaces is related to the solvation and hydrolysis (JAMES and LECKIE, 1972). When the ion approaches the surface, these terms can be related to the dielectric constant of the mineral (SVERJENSKY and SAHAI, 1996; SAHAI and SVERJENSKY, 1997). Molecular dynamics simulations

indicate that the dielectric field near the edges of goethite nanoparticles may be heterogeneous, leading to regions where ions are preferentially solvated (Rustad and Felmy, 2005).

The “intrinsic” free energy of adsorption, ΔG_{chem}° , will depend strongly on the properties of the sorbent and sorbate and is related to the strength of chemical bonds between them. The magnitude of this intrinsic free energy will depend on the distribution of electron density between the metal, surface, and nearby solution. The electron density distribution is in turn related to the number of metal-surface bonds, the atomic surface structure, and thus the geometry of the adsorption complex. On a heterogeneous surface, sites which are more energetically favorable will have lower ΔG_{chem}° , for example $\Delta G_{chem}^{\circ}(\text{step}) < \Delta G_{chem}^{\circ}(\text{terrace})$. In relation to the current study, it is hypothesized that the 7 nm hematite particles have a greater number of surface heterogeneities that are energetically favorable for Cu^{2+} sorption. The effects of “surface roughness” have often been suggested as a reason why electrostatic surface complexation models are not able to appropriately fit data (VENEMA et al., 1998). These surface features likely provide binding environments which stabilize the distorted coordination octahedron of Cu^{2+} . The onset of Cu^{2+} sorption at lower pH for 7 nm hematite particles than 25 nm suggests that binding environments which are not present in significant amounts on the larger particles are controlling the sorption behavior onto the 7 nm particles.

3.5. Nature of high-affinity Cu binding sites

Several studies highlight the complex and dynamic nature of hematite surfaces (see Introduction). What is the nature of the binding sites on the 7 nm particles that have

higher affinity for Cu^{2+} ? Many clues emerge from this work and previous investigations. It is now established that features such as edges, steps and adatoms give rise to most reactivity of surfaces in gas-phase reactions or in vacuum. At these sites, metal ions tend to exist in coordinatively undersaturated environments, where the coordination number of the metal is often lower than in the bulk (KNOZINGER, 2000). Several studies have documented increases in coordinatively undersaturated (or, “cus”) metal cations on the surfaces on nanoscale metal oxides, and a general principle seems to be that particles less than 10 nm begin to exhibit significant amounts of cus surface cations. For example, Zhang et al. (ZHANG et al., 2004) found that single crystal TiO_2 surfaces contained only 6-fold coordinated Ti, 6 nm particles had 33 % 6-fold and 67 % 5-fold coordinated Ti, and 2 nm particles had 100 % 5-fold coordinated surface Ti cations. Similar results have been suggested for Fe_2O_3 materials (CHEN et al., 2002; RAJH et al., 2002). The ab-initio study of Bergermayer et al. (2004) suggests the presence of tetrahedrally coordinated iron atoms at the hematite surface that can be stable under various pO_2 regimes. They relate the prediction of these undercoordinated iron atoms to the STM images of Wang (1998), and assign them a formal oxidation state of +5.

Different principles apply in solution, where oxygen vacancies are filled by reaction with water. However, surface ions are still affected by their bonding relationships to the mineral. Sites with crystal chemical variability are still generated near particle edges (RUSTAD and FELMY, 2005). Assuming that edges can be considered close-packed chains of O^{2-} ions with ionic radius of 0.13 nm, the percentage of edge O^{2-} ions relative to the total number of O^{2-} ions in the crystal is presented in Fig. 7. As the particle diameter becomes smaller than approximately 10 nm (assuming equal width:

height ratios to those measured by AFM), edges begin to contribute substantially to the particle surfaces. Considering that the 7 nm average diameter hematite sample used in this study actually contains a large percentage of the size distribution in this range, it is very likely that edge sites with variable Fe-O coordination exist in significantly greater proportion than would on 25 nm or 88 nm hematite particles.

3.6. Implications for reactivity of metal ions on hematite nanoparticle surfaces

The presence of these sites was hypothesized by Madden and Hochella (2005), who noted that faster oxidation of Mn^{2+} to Mn^{3+} on 7 nm hematite was consistent with the presence of binding environments which stabilize Mn^{3+} (distorted octahedron) relative to Mn^{2+} (perfect octahedron). Changes in metal binding environments clearly have implications for heterogeneous redox reactions, such as Mn^{2+} oxidation. In these cases, adsorption on the mineral surface either (or in some combination) breaks the metal coordination symmetry, donates electron density, and/or acts as an electron accepting electrode to promote the redox reaction (for example, the reaction between Mn^{2+} and O_2). Using in-situ Atomic Force Microscopy, it was observed that on hematite basal planes the MnOOH precipitates that form as a result of heterogeneous Mn^{2+} oxidation in the presence of O_2 always initiated at the base of steps (JUNTA and HOHELLA, 1994), and that the most accurate form of a rate law would explicitly include the distribution of topographic features (ie., binding environments) (JUNTA-ROSSO et al., 1997). Unfortunately, it is not always possible to have direct observations of all the crystal faces involved in a powdered sample, and even more difficult to make these observations on extremely small particles.

Other lines of evidence support the idea that changes in metal coordination have dramatic effects on metal reactivity. Previous studies of the effect of various ligands and aqueous complexes on metal oxidation rates illustrate an equivalent concept. For example, the rate of ferrous iron oxidation by O₂ is strongly dependent on the presence of complexing ligands. Linear free energy relationships have already been demonstrated between the rate of metal iron oxidation by O₂ and the equilibrium constant calculated from the free energy of reaction, specific to each aqueous and hydrolysis species (WEHRLI, 1990). In addition, there is a direct correlation between the difference in stability constants of ligands for ferric and ferrous iron and the ferric/ferrous redox potential (Table 1).

Fig. 8 shows the change in redox potential of iron complexes as a function of the quantity

$$\log K_{eq} \left(\frac{[FeL^{3-n}]}{[Fe^{3+}][L^{n-}]} \right) - \log K_{eq} \left(\frac{[FeL^{2-n}]}{[Fe^{2+}][L^{n-}]} \right), \quad (3)$$

which simply represents the stability of the complex for ferric vs. ferrous iron. Clearly, those complexes which stabilize ferric iron are poor oxidants; they resist the acceptance of an electron. In other words, those ligands encourage the transfer of an electron away from Fe²⁺. Because the coordination geometry and electronic structure of the iron-ligand complexes to the right of Fig. 8 are more suitable for stabilizing Fe³⁺, the Fe²⁺/Fe³⁺ half cell reaction occurs at much lower E_H than with ligands that stabilize Fe²⁺ (left side of Fig. 8).

These relationships between redox potential and coordination environment are directly analogous to the present study. Cu²⁺ ions are most stable in distorted octahedral coordination due to their d-electron configuration, as is also the case for Mn³⁺. On the

other hand, Mn^{2+} is most stable in a symmetric octahedral crystal field. Thus, binding of Mn^{2+} in distorted coordination environments on mineral surfaces stabilizes Mn^{3+} relative to Mn^{2+} , increasing the thermodynamic driving force for the manganese oxidation reaction.

5. SUMMARY

The use of Cu^{2+} as a probe metal for hematite nanoparticle surfaces has demonstrated the unique reactivity of nanoscale particles with diameters less than 10 nm. Specifically, the affinity of Cu^{2+} for hematite follows the order 7 nm > 25 nm = 88 nm. In agreement with recent spectroscopic evidence for metal binding on goethite-like nanomaterials (KIM et al., in preparation), it is suggested that distorted binding environments with reduced symmetry exist in increasing proportion on the surfaces of particles smaller than approximately 10 nm. These sites may be associated with particle edges or other topographic features. Size-dependent changes in the surface structure of nanominerals have implications for the unique reactivity that likely occurs with these materials in the environment, such as interfacial and redox processes.

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FIGURES

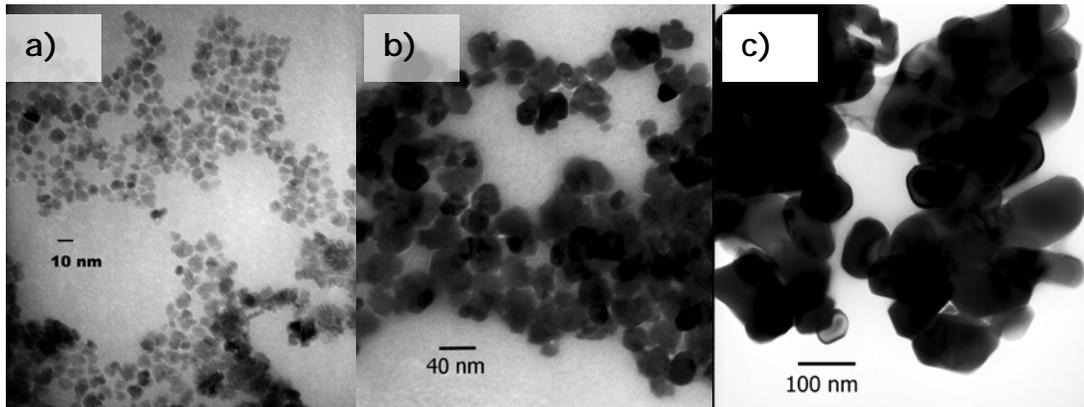


Fig. 1 – TEM images of the a) 7 nm average diameter, b) 25 nm average diameter hematite, and c) Fisherbrand 88 nm average diameter samples.

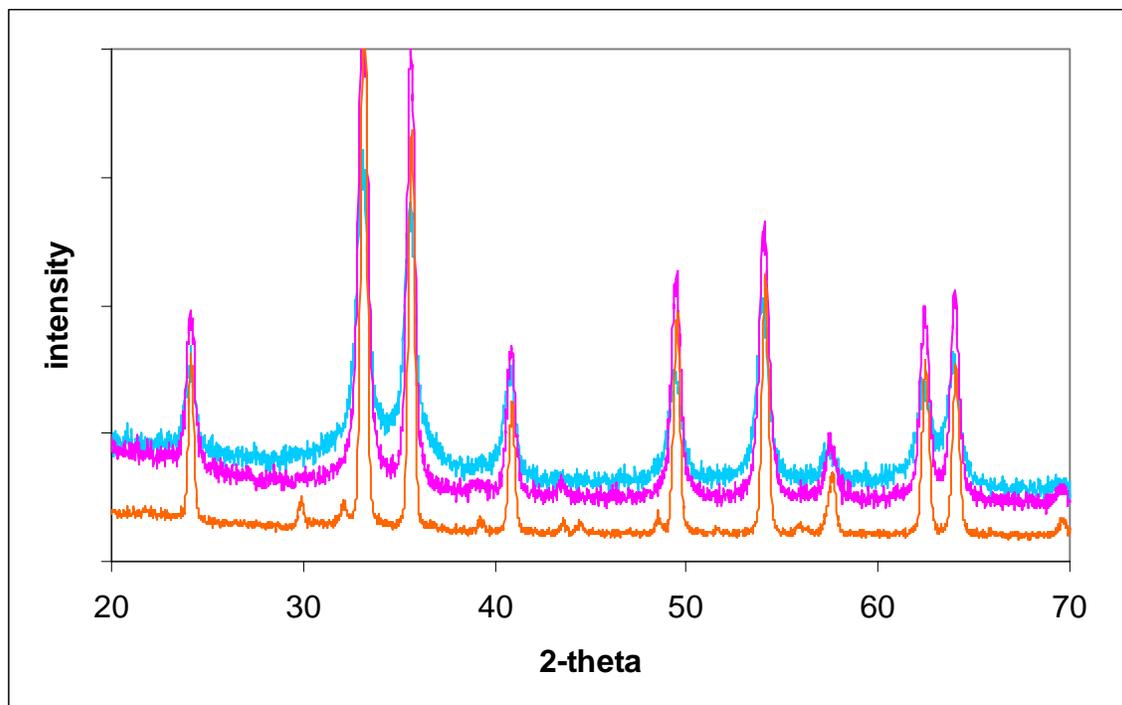


Fig. 2 – XRD patterns of 7 nm (higher background), 25 nm (middle), and Fisherbrand (88 nm, bottom) hematite.

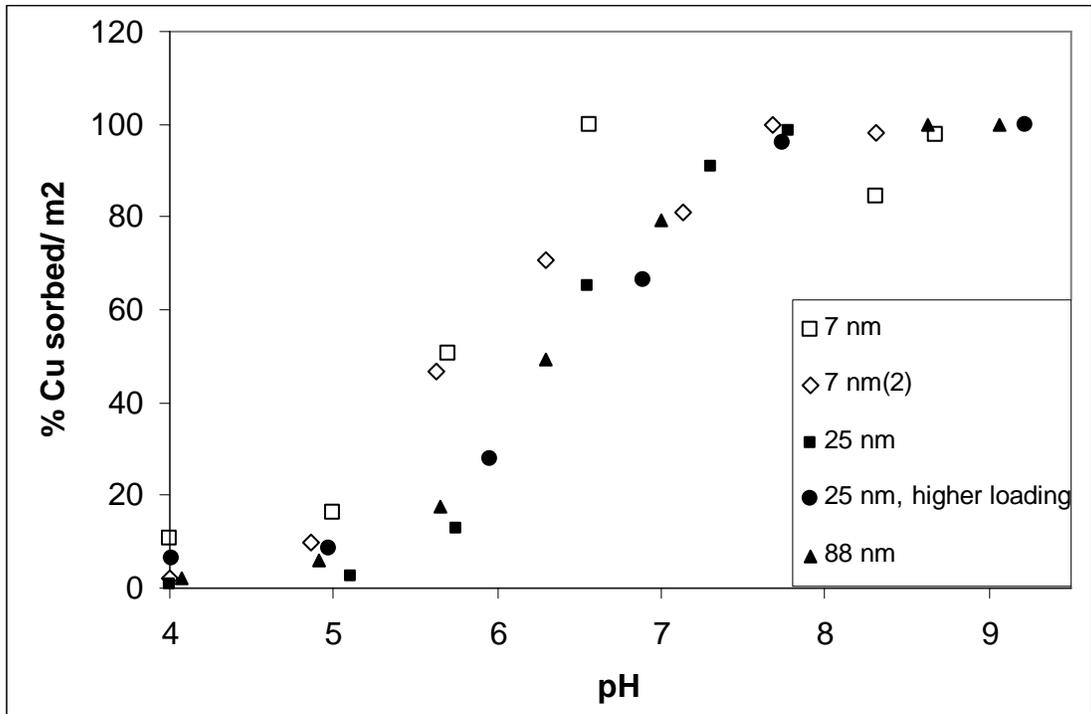


Fig 3. Batch Cu²⁺ sorption results.

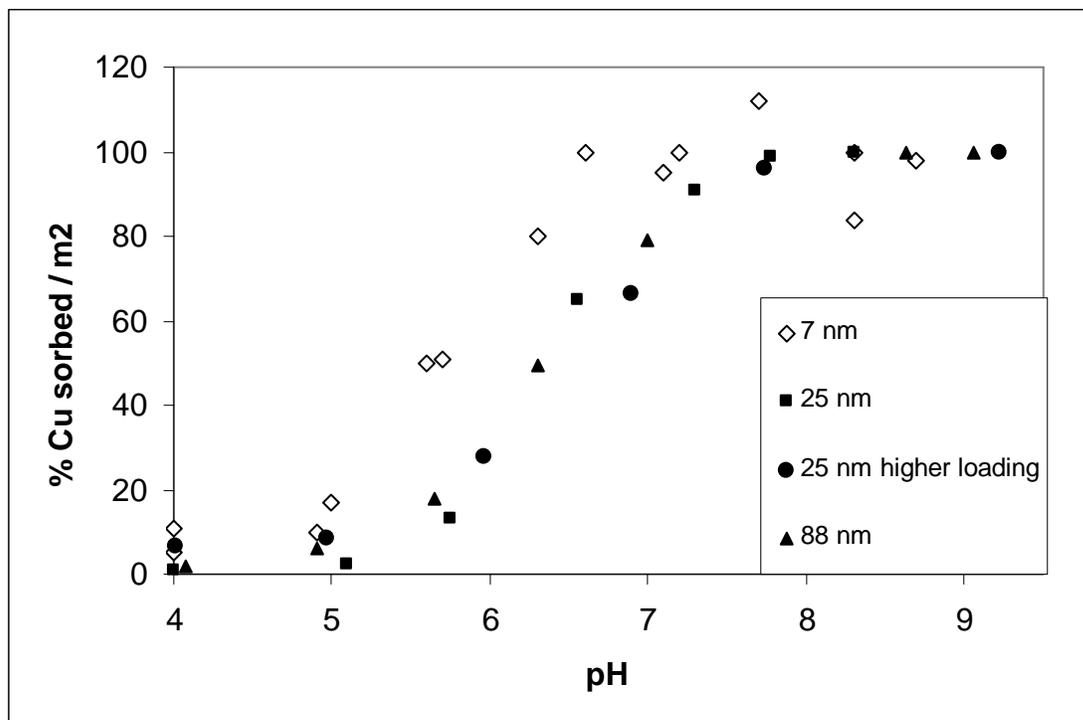


Fig. 4. Batch Cu^{2+} sorption results corrected for iron in analyte solution.

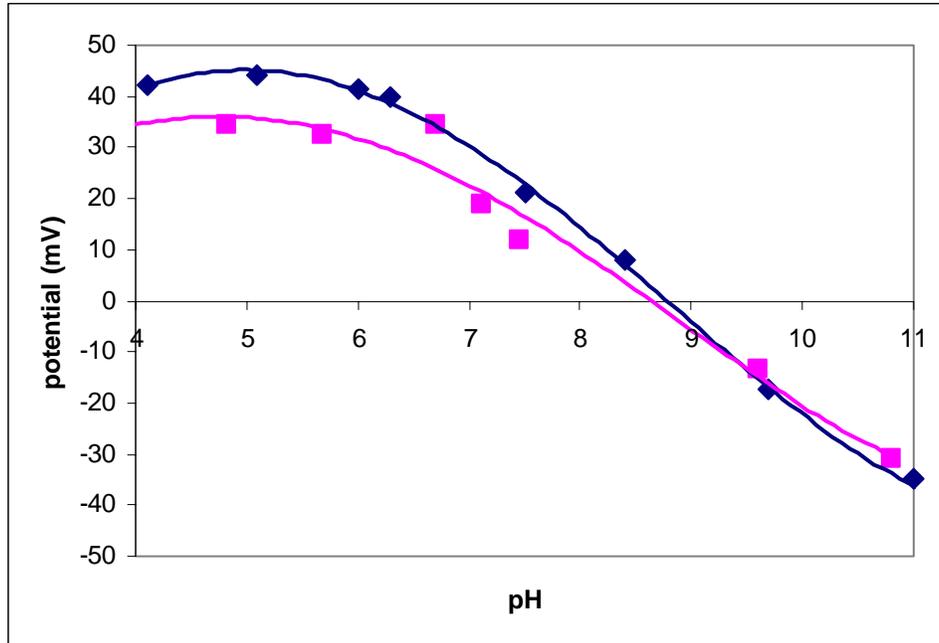


Fig. 5. Zeta potential data for 7 nm (diamonds) and 25 nm (squares) hematite.

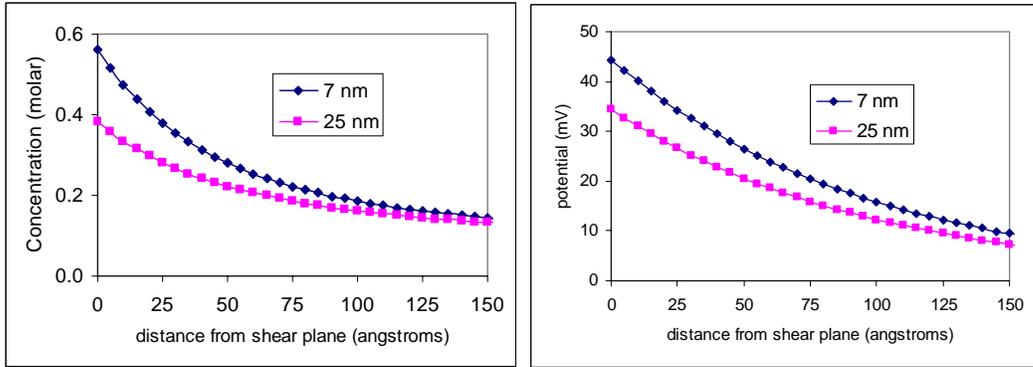


Fig. 6. Distribution of a) nitrate ions and b) surface potential as a function of distance from the shear plane, using measured zeta potential data and the Boltzmann equation. See text for details.

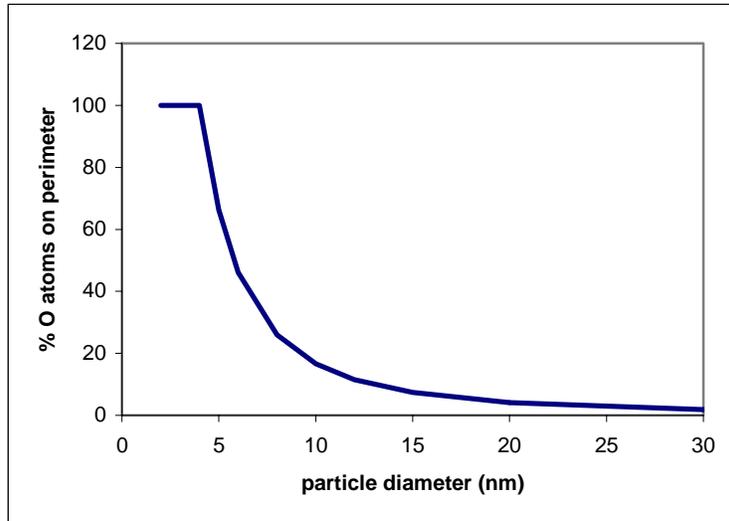


Fig. 7. Percentage of oxygen ions in the crystal calculated to be on the perimeter, assuming close-packing of 0.13 nm O^{2-} along the extent of the calculated perimeter, as a function of hypothetical hexagonal platelet diameter.

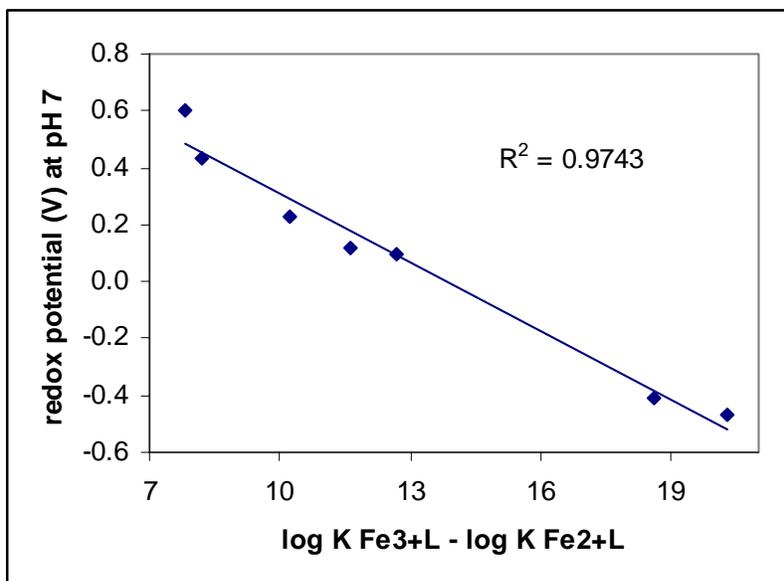


Fig. 8. Relationship between the preference of a ligand for ferric vs. ferrous iron and its redox potential.

TABLES

Complexant	log K, ferric	log K, ferrous	difference	Eh at pH 7 (V)	source
Desferrioxamine B	30.6	10.3	20.3	-0.468	a
Exochelin MS	28.86	10.1	18.76	-0.410	a
NTA2			12.7	0.100	b
EDTA	27.7	16.1	11.6	0.120	b
Salicylic acid	17.6	7.4	10.2	0.230	b
CN6	43.6	35.4	8.2	0.430	b
Citric acid	13.5	5.7	7.8	0.600	b

a = Dhungana and Crumbliss. (2005)

b = Stumm and Morgan (1996)

Table 1. Data for Fig. 6 (STUMM, 1996; DHUNGANA and CRUMBLISS, 2005).

ELECTRONIC ANNEX EA-1

sample	7 nm (1)	7 nm (2)	25 nm	25 nm	88 nm
volume (L)	0.4	0.4	0.5	0.4	0.5
g NaNO3	3.52	3.52	4.4	3.99	4.788
mol/L NaNO3	1.0E-01	1.0E-01	1.0E-01	1.2E-01	1.1E-01
mol/L Cu2+	4.55E-05	4.55E-05	2.93E-05	7.77E-05	2.93E-05
susp. density (g/L)	0.25	0.25	0.85	0.6	0.85
surface area (m2/g)	188	188	62	62	20
Total mol Cu2+	1.8E-05	1.8E-05	1.5E-05	3.1E-05	1.5E-05
mol Cu2+ /m2	9.67E-07	9.67E-07	5.57E-07	2.09E-06	1.73E-06

	pH	mol Cu sorb / m2	% sorbed	ppm Fe
7 nm (1)	4.0	3.56E-08	11	0.0685
	5.0	5.37E-08	16	0.017
	5.7	1.66E-07	51	<0.0027
	6.6	3.27E-07	100	<0.0027
	7.2	2.39E-07	73	0.0396
	8.3	2.75E-07	84	<0.0027
	8.7	3.20E-07	98	<0.0027
7 nm (2)	4.0	6.91E-09	2	0.4831
	4.9	2.92E-08	10	0.0299
	5.6	1.4E-07	47	0.0953
	6.3	2.11E-07	71	0.1391
	7.1	2.43E-07	81	0.2313
	7.7	2.99E-07	100	0.175
	8.3	2.94E-07	98	<0.0107
25 nm	4.0	1.02E-08	1	
	5.1	3.38E-08	2	
	5.8	1.78E-07	13	
	6.6	8.9E-07	65	
	7.3	1.24E-06	91	
	7.8	1.35E-06	99	
	8.3	1.37E-06	100	
25 nm higher loading	4.0	3.28E-07	7	
	5.0	4.20E-07	8	
	6.0	1.38E-06	28	
	6.9	3.31E-06	66	
	7.7	4.79E-06	96	
	9.2	5.00E-06	100	
88 nm	4.1	1.41E-07	2	
	4.9	4.12E-07	6	
	5.7	1.21E-06	18	
	6.3	3.37E-06	49	
	7.0	5.43E-06	79	
	8.6	6.85E-06	100	
	9.1	6.85E-06	100	

Nano2Earth

Introducing Nanotechnology through Investigations of Groundwater

**A Curriculum for Secondary —
Biology, Chemistry, and Earth and
Environmental Science Teachers**

**Andrew S. Madden, George E. Glasson, Michael F. Hochella, Jr., Susan C. Eriksson, Editors
NanoGeoscience and Technology Laboratory at Virginia Tech**



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Editors**



www.nanoed.vt.edu

2005

NanoGeoscience and Technology Laboratory
Department of Geosciences
Department of Teaching and Learning
Virginia Tech

The Nano2Earth Project - Nano2Earth (pronounced “nano-to-Earth”) is a science curriculum written for secondary schools. It brings nanoscale science and technology to life in the context of the Earth and environmental sciences. Nanoscale science and technology, combined to work with environmental science issues, transcends traditional scientific knowledge and processes presented in high school chemistry, biology, geoscience, and environmental science classes today. Nevertheless, every aspect of the curriculum addresses one or more of the National Science Education Standards.

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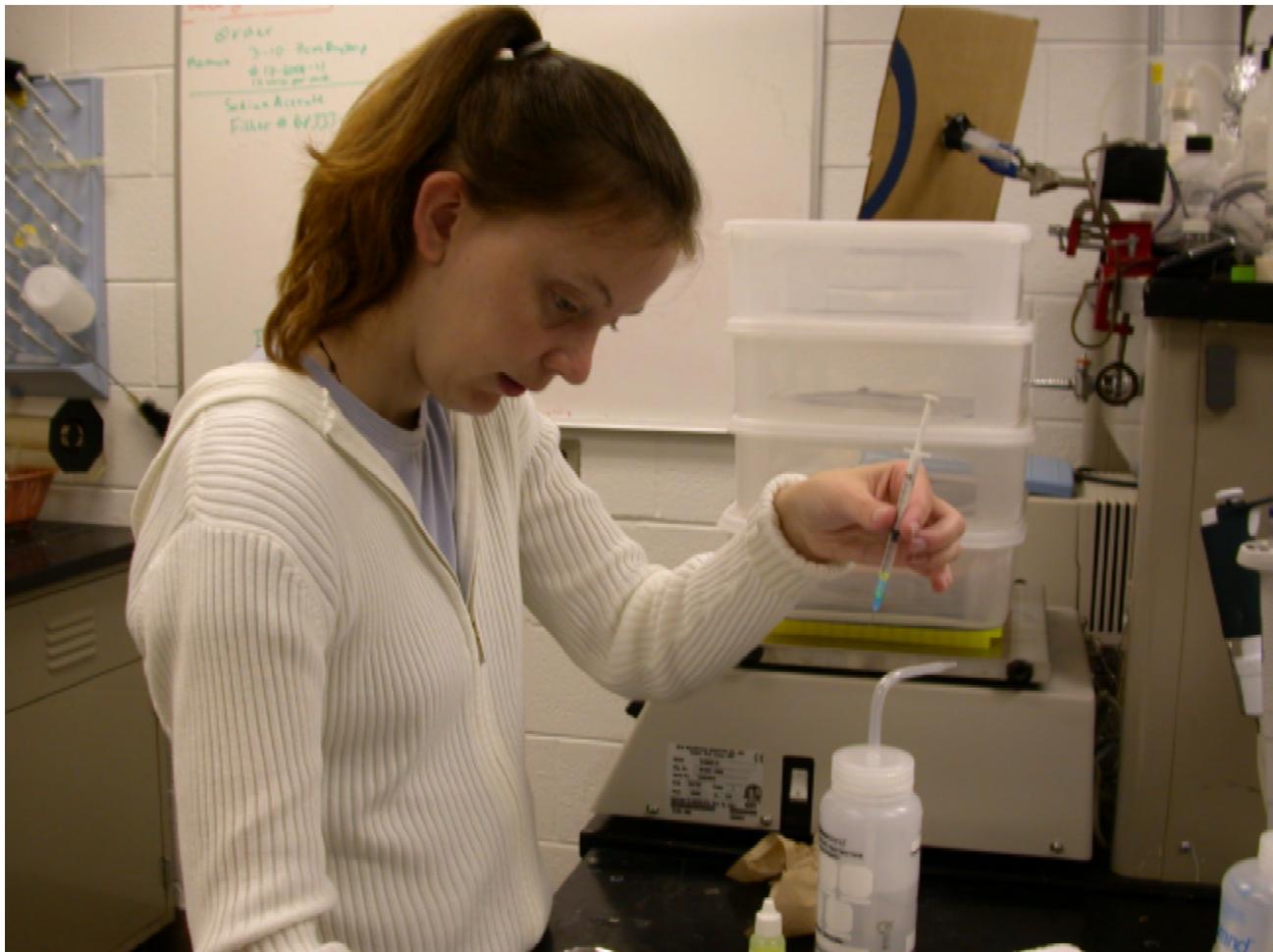
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Nano2Earth team member, Dr. Tracy Bank, prepares a solution of fluorescent microbeads while developing Lesson 4, "Investigation of Bacterial Transport in Groundwater."

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Graduate student, Andrew Madden, explains to the Nano2Earth team how nanoscale forces of interaction are related to the properties of mineral surfaces.

Preface

This is the first edition of Nano2Earth, a secondary school curriculum designed to introduce the new and revolutionary fields of nanoscience and nanotechnology to high school students. It is the first program in the country (as far as we know) to introduce these subjects using an environmental science approach, and, therefore, it is appropriate for biology, chemistry, and Earth science courses. Chapters 1 through 3 provide background material for the teacher, answering questions such as: What are nanoscience and nanotechnology? What are the important historical and societal aspects of nanotechnology? How is nanoscience related to environmental science? Following this, Chapter 4 describes how education in nanoscience and nanotechnology addresses the National Science Education Standards. Chapters 5 and 6 contain the curriculum itself. Teachers may use the entire curriculum, or pick and choose among its several parts depending on the emphasis they prefer, the level of their course, and the time that is available. The curriculum is meant to be entirely flexible, with numerous jumping in and exit points. Teachers can use aspects of the curriculum for as little as one day, the entire package for a few weeks, or any length of time in between.

Nano2Earth originated as an outreach project in the Department of Geosciences at Virginia Tech. This

first edition was a collaborative project four years in development, conceived, written, and classroom-tested by five high school science teachers from southwest Virginia, four professors from Virginia Tech, and several graduate students (see list of authors and contributors). Funding for the project was generously provided by a four-year grant from the Nanoscience and Engineering Program of the National Science Foundation in 2001.

The authors of Nano2Earth are grateful to the National Science Foundation (grant EAR-01-03053) for their generous financial support, Dr. Mike Rocco at NSF for his leadership of the Nanoscience and Engineering Program, and Ellen Mathena, Richard Godbee, and Mark Fortney for critical technical support.

Your comments and suggestions are encouraged and should be sent to Ms. Ellen Mathena (mathena@vt.edu). These will help us produce the second edition of Nano2Earth. In addition, questions concerning the use of this curriculum should be sent to Ellen for distribution to the appropriate faculty member.

Nanotech's fear factor

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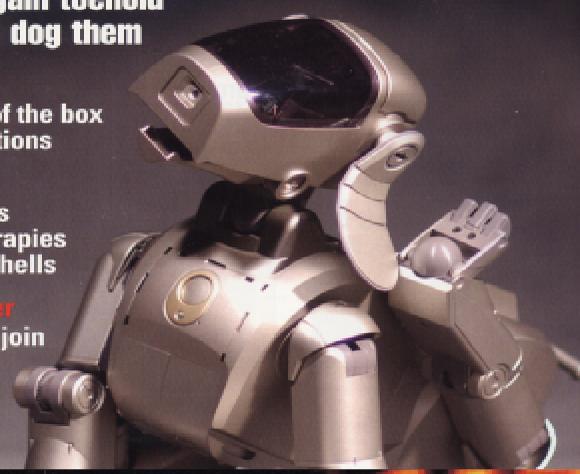
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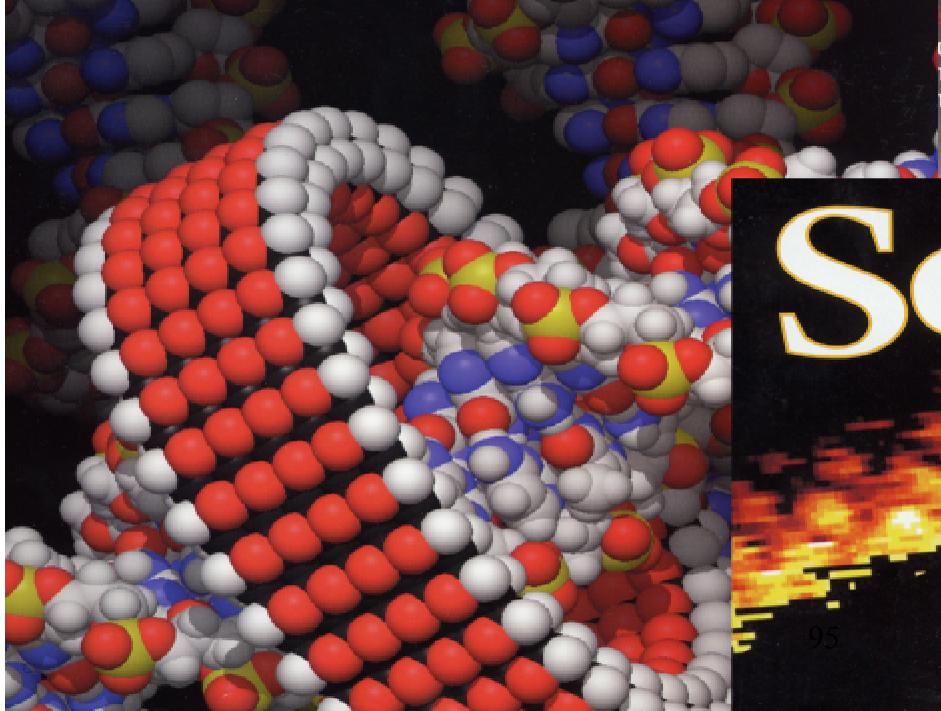
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What are Nanoscience and Nanotechnology?

A Nano Primer



Nano2Earth



1

The prefix “nano-” simply means one billionth of a meter. So, one nanometer is 10^{-9} meters. To help put this in perspective, one-tenth of one nanometer is approximately the size of an atom. For example, ten gold atoms, lying side by side, would be about one nanometer long. So why should a fundamental branch of science, indeed applicable to all sciences, be named after the “nano-” prefix? What is so special about this length scale? The answer lies in the physical properties of any substance that is this small. Let’s consider the melting point of gold. Look up this property in any reference book for metals, and you will find that gold’s melting point is listed at exactly 1064°C (1947°F). This temperature can be easily verified by placing a gold nugget in a high temperature furnace and ramping up the temperature. When this temperature is reached, the nugget changes shape and forms a ball of liquid gold. Now, let’s try the experiment again, but this time, instead of a gold nugget that we can see and easily handle, let’s melt a nugget that is only a few nanometers in diameter (obviously, we’ll need special equipment and methods to pull this off, but it can be done). Surprisingly, the melting temperature recorded in this case is only 427°C (800°F). Have we made a mistake? More experimentation would show that no mistakes had been made, and in fact we would find that the melting temperature of gold particles depends on the size of the particles that are being heated.

So why do all the reference books list 1064°C (1947°F) as the melting temperature of gold? This is because, for all practical purposes, this melting temperature is accurate. If we continued our melting experiments with a range of gold particle sizes, we

would find that all the gold particles melt at this temperature, from large nuggets to the smallest ones we can see. Only when the nugget size is reduced to several tens of nanometers would we start to measure a lower melting temperature. In fact, we would observe that in this size range, the smaller the particle, the lower the melting temperature.

This example allows us to easily and precisely define nanoscience and nanotechnology.

Nanoscience is the field of science that measures and explains the changes of the properties of substances as a function of size. Like the melting of gold, the properties of any substance will remain constant as its size gets smaller and smaller, that is until the size is reduced into the nanorange (depending on the substance and the property being measured, roughly 10 to 100 nanometers). In the dimensional nanorange, any physical property measured will continuously change with size, and often dramatically so. **Nanotechnology** simply takes advantage of this phenomenon by applying property modifications of this nature to some beneficial endeavor - and what a warehouse of beneficial endeavors there are! As described in the next chapter, the promise of nanoscience is so great and the application of nanotechnology so vast that they are projected to change our world, much as the biological revolution in genomics is presently changing it.

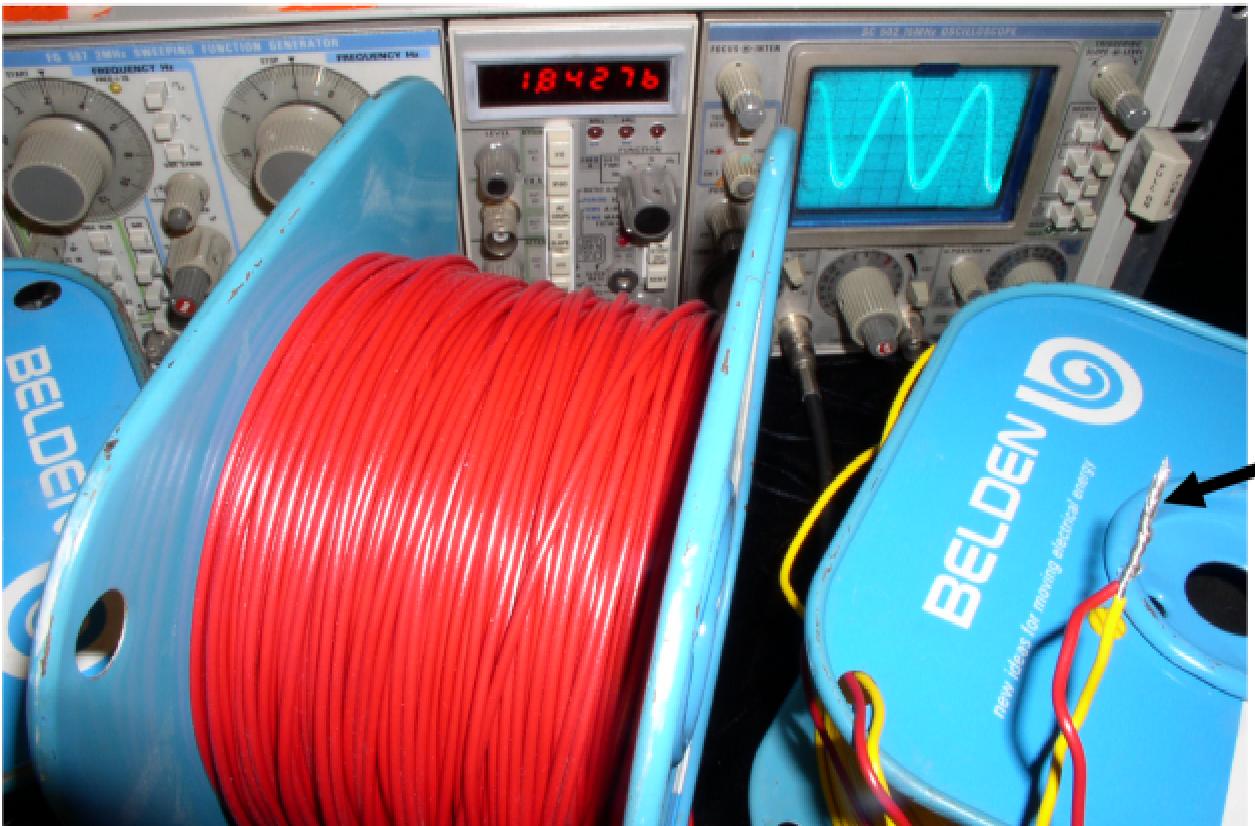
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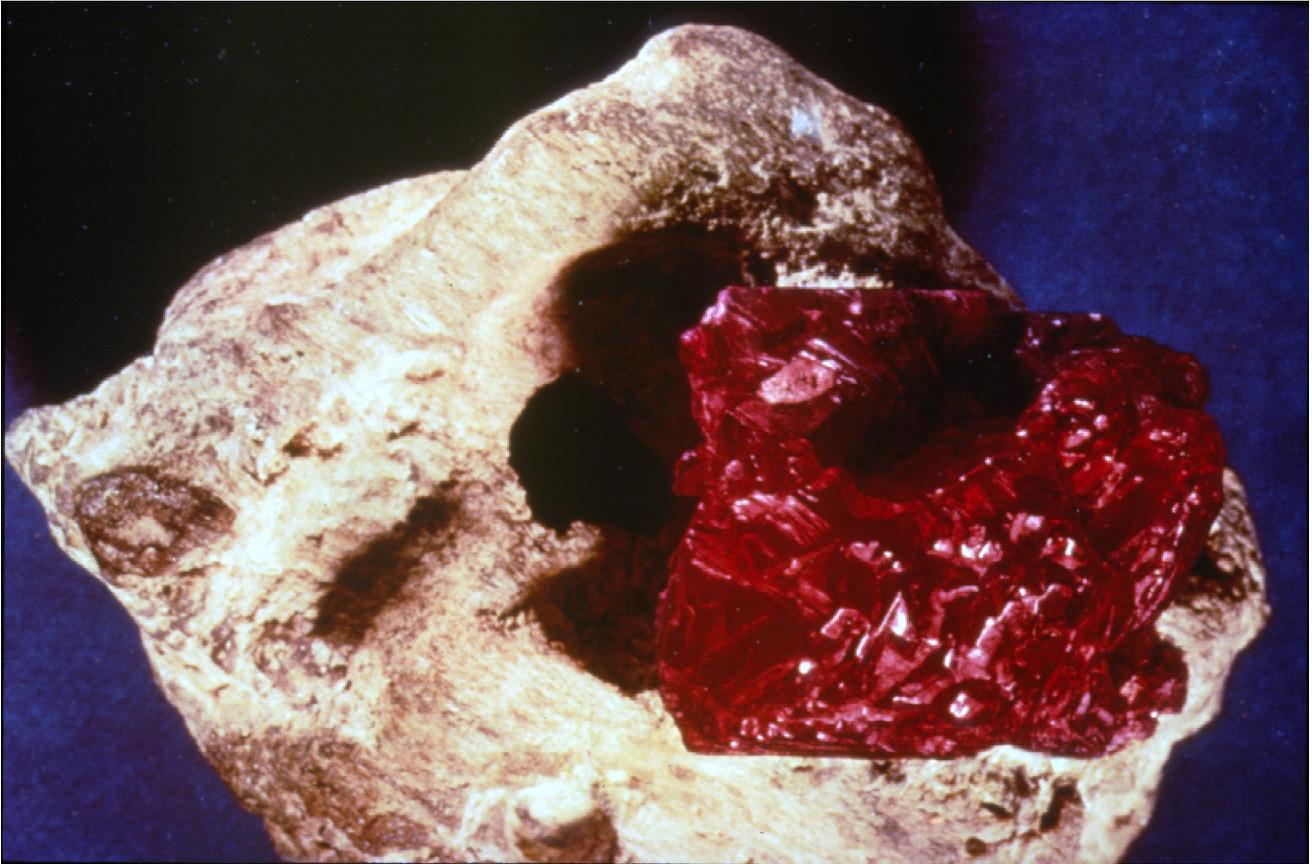
Opposite Page: A collage of recent magazine covers reporting important advances in nanoscience and technology. “smalltimes” is the industry’s trade journal, while “American Scientist” and “Science” often report on technical aspects of the most recent breakthroughs.

It is everyone's common experience that two aluminum wires twisted together (arrow) provide excellent electrical conduction from one wire to the other. Yet the aluminum metal wires are covered with aluminum oxide, an insulator. How is good electrical conduction achieved through the non-conductive aluminum oxide. Nanoscience explains this phenomenon.

It is important to realize from the outset that all substances show property changes through the nano-size regime. This includes solids, liquids, and gases. In addition, not all three dimensions of the substance need be in the nanorange. For example, a nanoparticle (like our small, low-melting temperature gold particles described above) is small in all three dimensions. What if we simply confine one dimension to be in the nanorange? With two dimensions unlimited, and one confined, we have created a nanofilm, that is a film with a thickness in the nanorange. Will its physical properties be affected relative to the same substance with no size restrictions? Absolutely, and let's use another example to illustrate this. Imagine that you have two wires made of aluminum, a metal that we know well as

electrically conductive. Imagine connecting each wire to the terminals of a battery, and then touching the surfaces of the wires together. Naturally, a circuit is formed and an electrical current will flow from one wire to the other. However, the surface of the wires is not conductive aluminum (Al) as one might assume, but in fact a thin film of aluminum oxide (Al_2O_3) which covers the aluminum metal. This is because the surface of aluminum, whether the aluminum is making up a wire, a soda can, or an airplane wing, oxidizes in air to an aluminum oxide. The apparent problem in our electrical conduction experiment is that aluminum oxide is a well-known insulator; that is, it does not conduct electricity. So how can a current flow from one wire to the other? The answer lies in the physical





One of the most valuable of all gemstones, blood-red ruby, is aluminum oxide with the same composition as the thin film which covers aluminum wire. Rubies do not conduct electricity, but the thin film of the wire does thanks to the special properties of nanofilms.

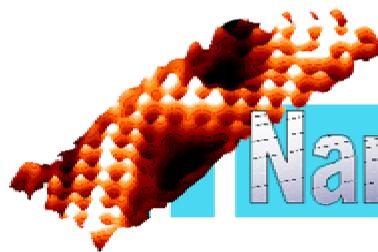
dimension of the aluminum oxide thin film. The coatings on the aluminum wires are very thin, typically on the order of one nanometer thick. In this size range, as we might expect, the electrical properties of the aluminum oxide have changed. When conducting electrons perpendicular to the thin film (that is across the film from one wire to the next), the aluminum oxide acts more like a conductor, and, therefore, the electrons are free to pass from one wire to the next. In other words, just due to the dimensions and geometry of the aluminum oxide, it effectively behaves more like a conductor than an insulator, and good electrical contact between the two wires is the result. Although this is something we take for granted, or in fact were never aware of in the first place, it is a dramatic result.

One simply needs to imagine what electronics would be like if bulk properties also applied to thin films!

In summary, in the examples presented above, we have defined the nanoscale and nanoscience. We have seen surprising results for two “ordinary” phenomena that we thought we knew everything about, but which were both shown to have surprising twists. These deceptively simple twists are what the nano-revolution is all about. This revolution is described in the next chapter.



Historical and Societal Aspects of Nanoscale Science and Technology



Nano2Earth



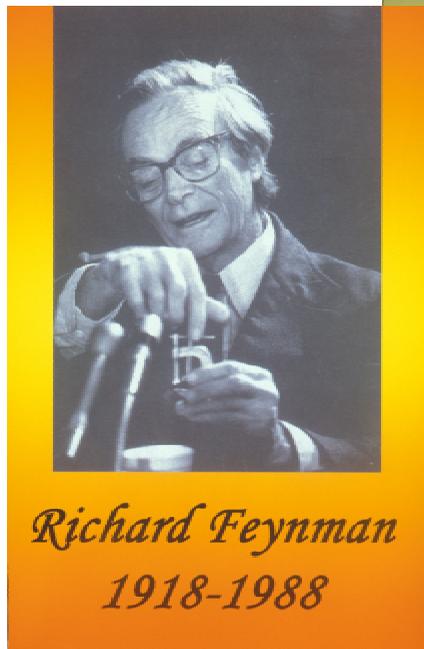
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What Was the Origin of the Terms Nanoscience and Nanotechnology?

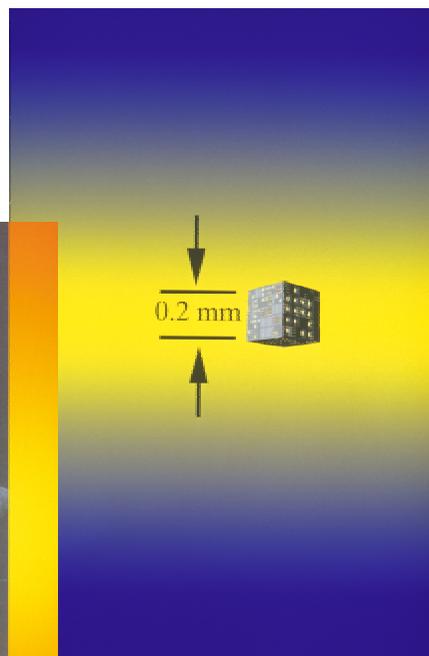
Nanoscale science is typically defined (for reasons given in Chapter 1) to be relevant between one nanometer and a few tens to perhaps one hundred nanometers. With the advent of X-rays in the late 1800's, crystallographers were working at the nanometer scale or smaller as atomic arrangements in crystals were first determined in 1912. But scientific historians do not point to the earliest beginnings of nanoscale science and technology until 1959, the year that Richard Feynman, a quantum physicist and one of the 20th century's greatest scientists, gave a speech to the American Physical Society entitled "There's Plenty of Room at the Bottom." Feynman was fascinated by the notion of scaling; and in this speech, he imagined that a single bit of information could be stored in a nanospace (specifically a 125 atom cluster), an exceptionally bold

prediction at that time. At that scale of miniaturization used for the encryption of alphabetic letters, he estimated that all the text ever written in books in the history of the world could be stored within a cube 0.2 millimeters on a side (and thus his lecture title). His

genius was not this, but his realization that "all things do not simply scale down in proportion," a point that is discussed in Chapter 1 and is now considered the cornerstone of nanoscience. What he was predicting was that as one scaled things down into the nanometer size range, materials would behave differ-



Richard Feynman
1918-1988



ently, and that this could be turned into an advantage. Near the end of his talk, he posed the ultimate challenge of matter when he said: "I am not afraid to consider the final question. Can (we) arrange atoms the way we want, all the way

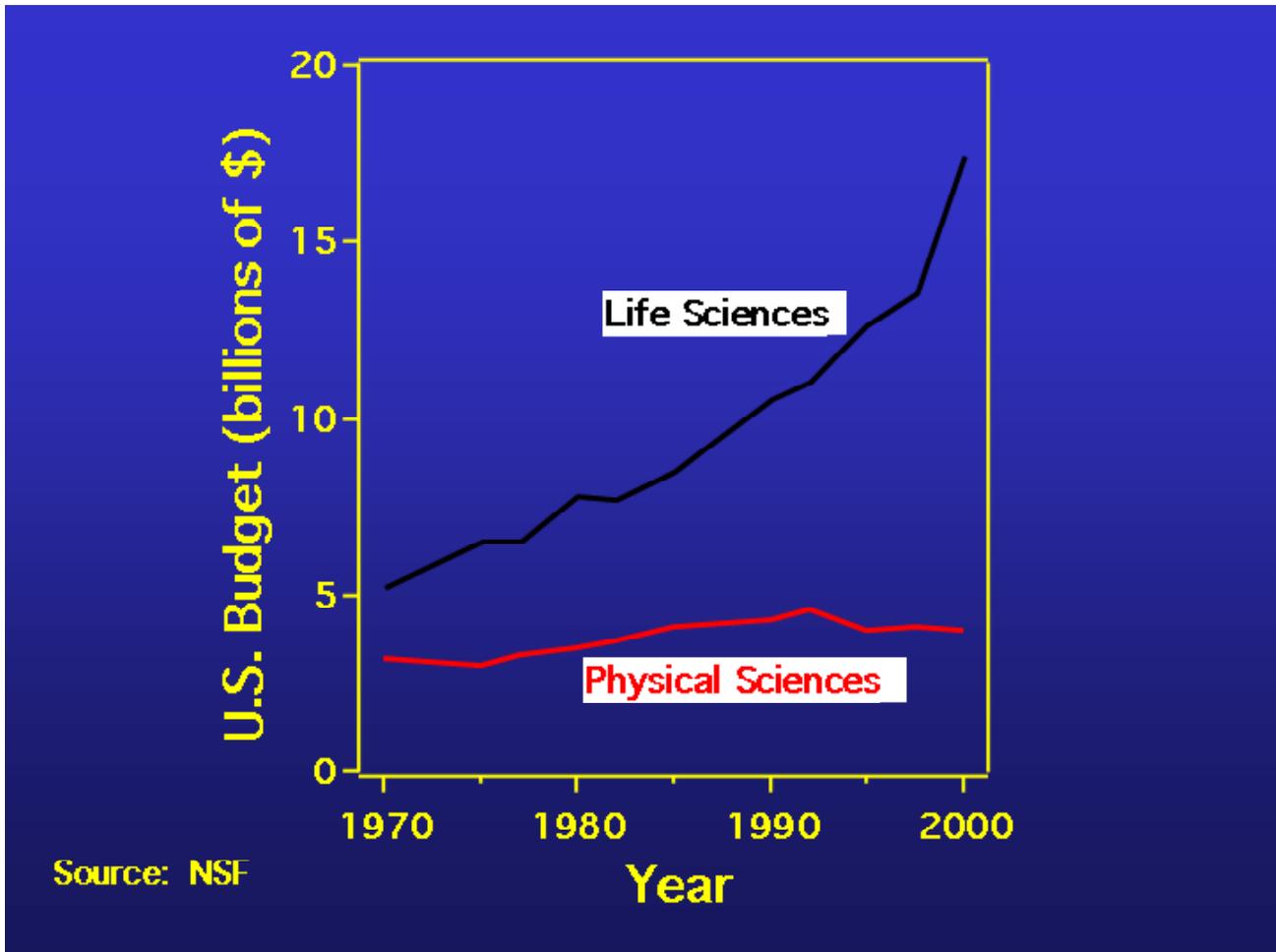
down?” The general reaction to his comments was amusement, as statements like these were considered scientifically radical, not necessarily visionary. For example, one of the great theoretical physicists of the last century, Erwin Schrödinger, predicted in the 1950’s that we would never experiment with just one atom or molecule. In reality, this feat took three more decades. In the late-1980’s, the direct manipulation of individual atoms by humans became a reality. Unfortunately, Feynman did not live long enough to witness this monumental achievement.

How Much Interest Has Nanoscale Science and Technology Attracted?

Few would argue that governmental funding increases in the medical sciences are

inappropriate. What many believe to be the problem is that as this funding has tripled (after adjusting for inflation) over the last 30 years in the United States, the funding for the physical sciences has remained essentially flat over most of the same period. However in 2000, the National Nanotechnology Initiative (NNI) was launched by the Clinton administration with great fanfare. Similar programs had already been initiated in other countries. At least in this sector of the physical sciences, the funding is increasing at an exceptional rate. Just two years after the beginning of NNI, the total annual expenditures were nearly \$600 million in the United States with by far the largest portions going to three

Federal funding of science in the United States from 1970 until 2000 according to the National Science Foundation



agencies, the National Science Foundation and the Departments of Defense and Energy. In 2005, the NNI funding level is expected to approach \$1 billion; the world's cumulative research and development expenditures will exceed four times this; and the corporate world is not about to be left behind. In several cases, they are leading the race. Giants such as IBM, Motorola and Dow Chemical are investing hundreds of millions of dollars in nanoscale science and technology. As important, hundreds of relatively small, high-risk start-up companies have been founded. Such funding shifts have not been seen within the physical sciences for many years, and the dramatic increase in funding nanoscale science and technology by the U.S. and other governments is just another indication of the young, but clearly recognizable revolution of which we are a part.

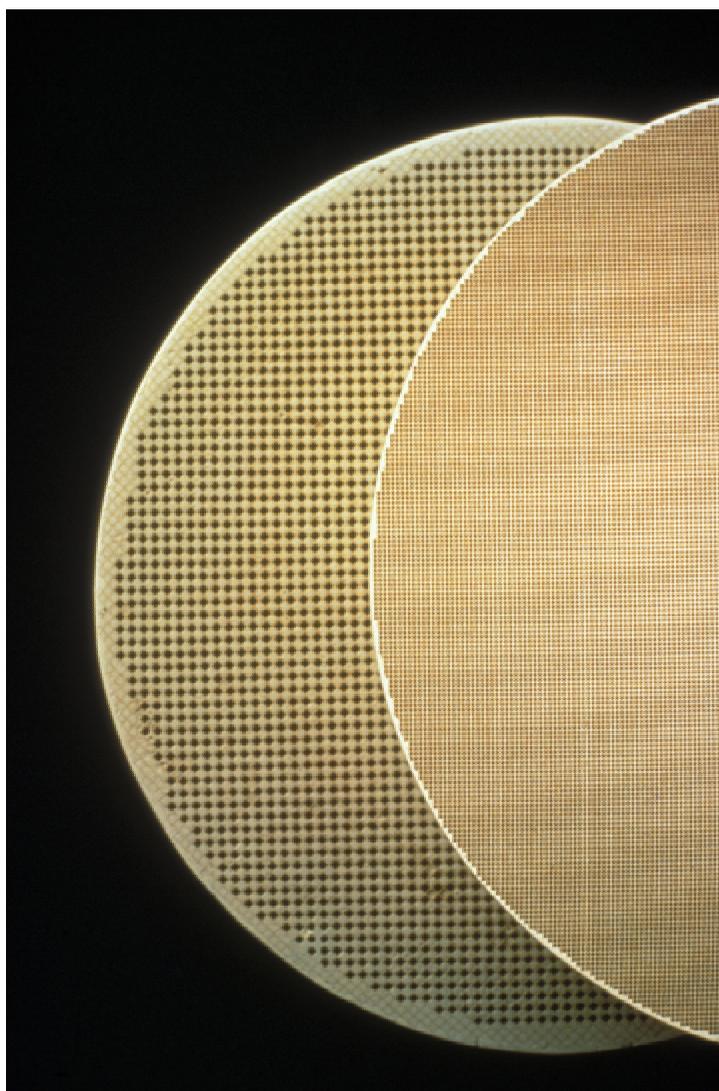
How Has Nanotechnology Already Affected Our Everyday Lives?

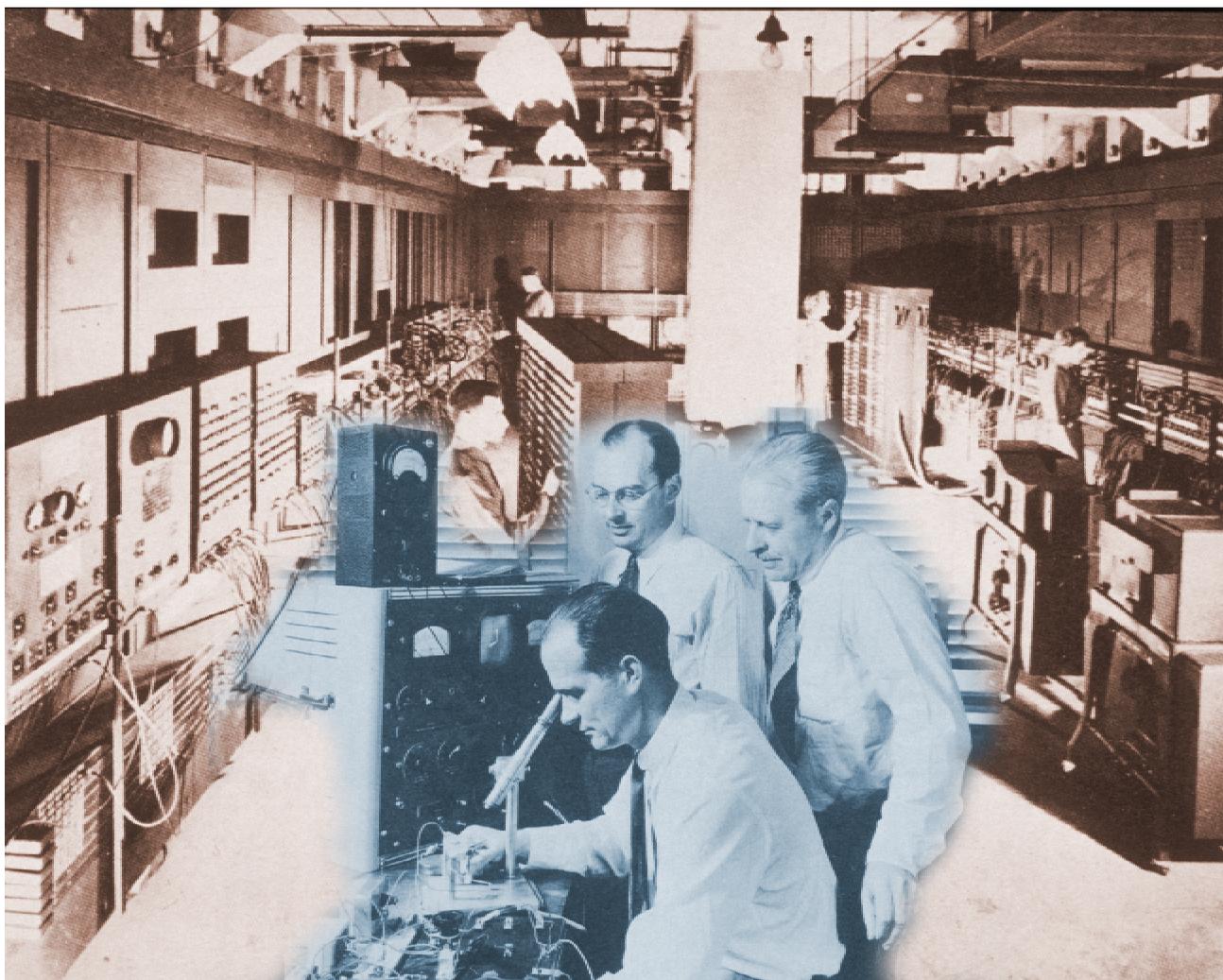
Before the "nano" label became so popular just a few years ago, scientists and engineers were hard at work developing useful products that use nanoscale particles and films with properties specifically targeted for a great variety of purposes. Nano-sized particles of zinc, cerium and indium oxides are already used in electronics, optics and personal care products like sunblock and cosmetics. Stain and wrinkle resistant pants sold by Eddie Bauer, Lee Jeans, The Gap, and other retailers use nanotech fiber and coating technologies.

In the computing world, nanotechnology is already having an important impact in disk data storage. Very recently, computer disk drives were quickly approaching the theoretical limit in data density for the existing technology of magnetic storage (20 to 40 gigabytes, or GB, per square inch), but with nanotechnology came the first major change in hard disk media materials and design in some time. In this process, on the surface of

a disk, a nanofilm of the metal ruthenium, only three atoms thick, is sandwiched between two much thicker magnetic layers. This allows stable magnetic domains in the layers above and below the ruthenium to be much smaller than previously obtainable while remaining stable over time. As a result, data may be stored at much higher densities, already allowing for 400 GB desktop drives (equivalent to the data on 80 DVD's or 600 CD's), 200 GB drives in notebook computers, and 6 GB drives in handheld devices. Although even these numbers may be obsolete in a few years, the point is that nanotechnology

Automotive catalytic converters produced by Corning, Inc. Nanoparticles of platinum or rhodium reside on the surface of the honeycomb ceramic structure. As hot exhaust gases pass through the channels, toxic nitrous oxides and carbon monoxides are converted to nitrogen and carbon dioxide gases.





In the background is ENIAC, the first fully operational large-scale electronic digital computer with its 18,000 vacuum tubes, 70,000 resistors, and 10,000 capacitors (Philadelphia, 1948). The inset in the foreground shows William Shockley (sitting) and John Bardeen and Walter Brattain (standing behind) in the same year shortly after their invention of the solid-state transistors that would lead to modern computers.

provided the quantum leap in disk design needed to continue to move this vital industry forward.

The most sweeping application of nanotechnology in the past can be found in the heterogeneous catalysis industry. Hidden away so that few are even aware of their existence, heterogeneous catalysts promote chemical reactions on surfaces and nano-size particles. This technology has played a key role in leading a multi-trillion dollar chemical industry worldwide, and the technology is used in literally hundreds of applications, from the refining of oil to the breakdown of toxic car emissions, the latter the work of catalytic converters.

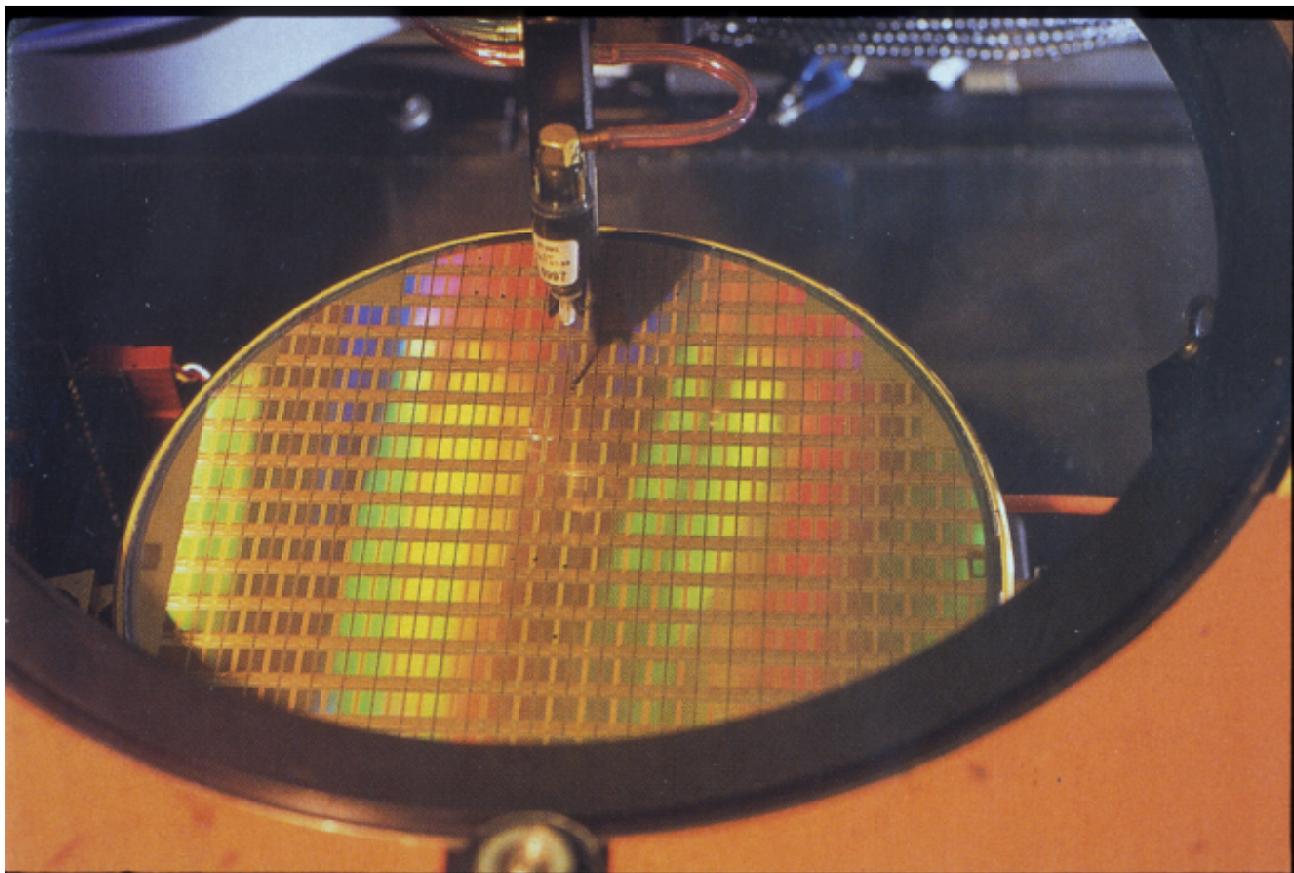
What Could Nanotechnology Mean to Society in the Long Run?

According to the National Science and Technology Council, nanotechnology “stands out as a likely launch pad to a new technological era because it focuses on perhaps the final engineering scales people have yet to master.” For example, it is widely anticipated that the future impact of nanotechnology will eventually far exceed the impact of the silicon-based integrated circuit (i.e., computer technology as we know it today). This is because nanoscience has applications in all areas of science, and nanotechnology has applications to all fields of technology, including robotics,

engineering, medicine, computing, and so on. Like the present biological science revolution in genomics, proteomics, and other health-related sciences, the importance of nanoscale science and technology is so sweeping, so vast, that no boundaries can yet be reliably defined, and no limits can yet be clearly foreseen. Scientific historians know all too well that technology predictions are notoriously inaccurate. In the March 1949 edition of the still popular and respected magazine *Popular Mechanics*, appearing shortly after the invention of the solid state transistor at Bell Labs (the invention that made modern computers a reality), experts published predictions of futuristic calculators (computers) that would add 5,000 numbers per second and weigh only 1,400 kg or so while consuming 10 kW of power. Today, a 1 kg laptop can add millions of numbers per second using about 1 W of power. So who can reliably say today

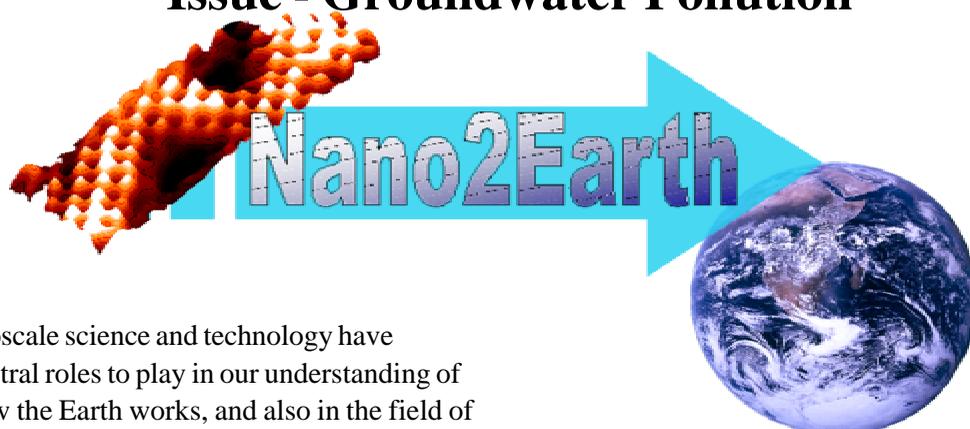
what a quantum computer, built from the bottom up using nanotechnology, will be able to do in the future, or what fields will be most dramatically impacted by nanoscience in the future? Besides unimaginably powerful computing devices, one can easily anticipate great advances in medical diagnostic tools, chemical sensors, communication devices, environmental restoration methods, construction materials, and cancer treatments, just to name a few. It is this small scale – the ability to put molecules and atoms to new uses – that fuels the hope and hype surrounding nanotechnology. What seems certain is that nanoscale science and technology will make a lasting impact on every scientific field, in every area of modern technology, and as a result, in our daily lives.

An eight-inch diameter “wafer” of modern computer chips, before they are separated to go into individual machines or computers. Each silicon chip may contain as many as tens of millions of solid state transistors.





The Link Between Nanoscale Science, Technology, and a Vital Environmental Issue - Groundwater Pollution



Nanoscale science and technology have central roles to play in our understanding of how the Earth works, and also in the field of study that we call environmental science. Natural substances that exist with at least one dimension in the nanometer size range, from both living and nonliving systems, are everywhere. Key chemical reactions occur on, within, and around these substances. In addition, new types of sensors and detectors based on rapidly emerging nanotechnologies are having major impacts on how we model and understand important natural reactions that influence the environment. Student investigations described in this curriculum touch on all of these concepts.

The curriculum described in this book introduces nanoscale science and technology through investigations of groundwater pollution. Groundwater is second in abundance as a freshwater source only to water found in glaciers and polar ice. It is critically important as a freshwater source to much of the Earth's population. Yet, when it is polluted, it becomes a severe and dangerous liability with literally hundreds of millions of lives at stake from waterborne illnesses.

This chapter provides teachers with critical background information on the nature of groundwater, and why nanoscale science and technology are so relevant to groundwater pollution.

The “Critical Zone” of the Earth

The critical zone of our planet is the place where the land meets the fluid envelopes of the Earth, the hydrosphere and atmosphere. It is the place where we live, and it is the place that provides us with fresh water, agriculture, and many vital natural resources such as soil, timber and many mineral deposits. Considering all the geo- and bio-aspects of this zone, it is probably the most heterogeneous and complex portion of the entire Earth. Understanding it as best we can is an important key to intelligently sustaining this planet for human habitation.

Earth processes within the critical zone can be conveniently divided into three principal and overarching categories based on the physical, geochemical, and biological processes that occur there. All of these categories are strongly cross-linked, each one affecting the others to various degrees. They are

- biological activity, which, due to organism nutritional requirements, drives a significant amount of the chemical cycling within and between water, soil, rocks, and the atmosphere
- weathering (the breakdown of minerals), which is constantly at work in the critical zone generating soil, producing mineral by-products in the process, and redistributing elements among water, rocks, and organic materials

- fluid transport, the critical component in water resources supply and management, as well as everything from flooding to landform development

Below, we will look at a few of these critical zone processes. This will act as an introduction to the curriculum found in the remainder of this book.

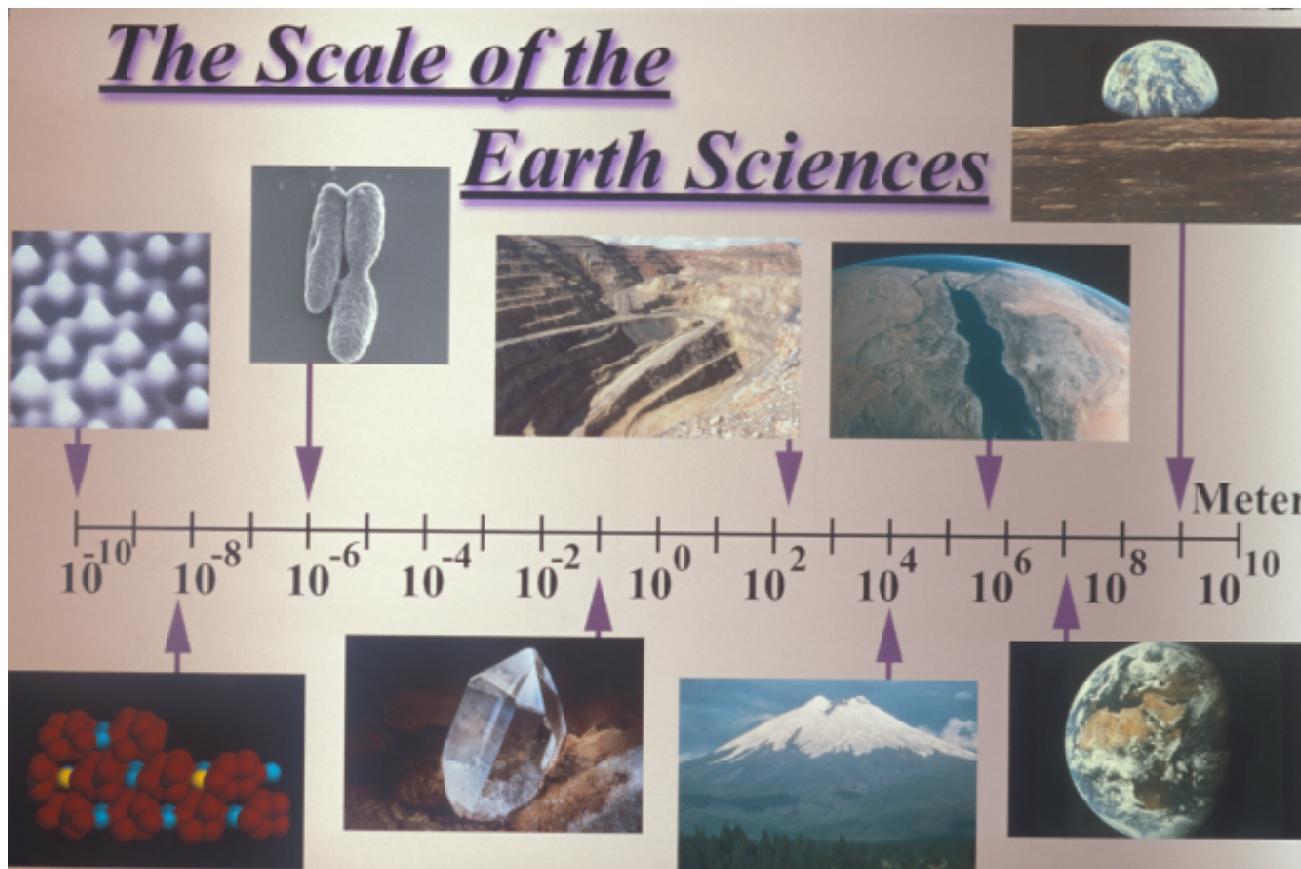
The Earth-Moon system has a dimension of 10^9 meters, but the inner space of this system is more vast than its outer space. At 10^{-10} meters, we are in the realm of atoms as seen in this figure by scanning tunneling microscopy (far left image; Pb and S atoms on a galena – PbS – surface).

Water/Mineral/Bacteria Nanoscience

Nearly all aspects (both geo- and bio-processes) of weathering, soil, and water/rock interaction sciences are inexorably linked to nanoscience. Within the Earth’s near-surface, materials that are broken down, as well as materials that are produced, are often in the size range of nanometers. Further, as organic molecules, simple and complex, as well as bacteria and all flora and fauna in soils and rocks, interact with the mineral components present, nanodimensions and nanoscale

processes are the order of the day. If one does not know what is going on at this scale, one can by no means have the complete picture of these exceptionally complex systems.

The biggest scientific problem is that one needs to know how things work at this small and awkward scale in the first place. The reason that one needs to know this is because processes that occur at the micron (one millionth or 10^{-6} meters) and larger dimensions, making them easier to see and study, simply do not scale down to the nanoscale (one billionth of a meter or 10^{-9} meters). Within the nanoscale, as we first mentioned in Chapter 1, entirely different processes are possible; processes found nowhere else in the dimensional range of the Earth.



One of the most important interactions in the weathering environment and in soils is mineral-bacteria association. The bacteria, typically in the micron-size range with dynamic membranes of physiological suites of organic molecules, interact with surfaces of any one of thousands of minerals, each with their own chemistry, atomic structure, and topography. This interaction takes place over nanometers of distance as their surfaces approach one another, are in contact, and separate. Recently, all of these forces of interaction, between fully viable (normally functioning) bacteria and various mineral surfaces in water, have been quantitatively measured in real time using a variation of atomic force microscopy, or AFM. Measurements of this type speak to the heart of nanoscience, insofar as the observer is looking at nanoNewtons of force over nanometers of distance. As a bacterial cell and a mineral surface are brought closer together, the confined water layer in between is subject to the same consequences of any nano-sized substance, influencing and influenced by the macromolecular outer cell envelope of the bacterium and the mineral surface. This aspect of nanoscience will have applications to bacterial transport. For example, if the bacterium attaches to a mineral surface, it is effectively removed from groundwater flow. If it does not attach, it is transported with the groundwater flow; and this is of great concern if that species is pathogenic, that is, disease-producing. Bacteria attachment dynamics is also of great interest in subsurface in-situ bioremediation - the use of wastewater for irrigation or for groundwater recharge, and many other issues pertaining to mineral-microbe interaction.

Metal Transport Nanoscience

Metal transport in the environment is often a serious environmental problem,

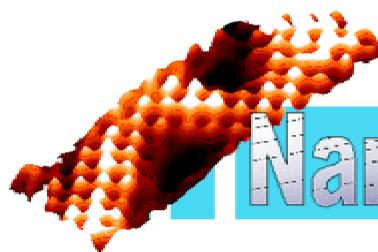
whether related to radioactive waste disposal, natural movement of toxic metals, industrial pollution, or any number of other scenarios. Metal mobility ultimately depends on

- the chemical reactivity of the metal in question as dictated by bonding characteristics and interactions
- the part of the environment through which transport occurs (e.g., soil, groundwater, surface water, atmosphere)

A fundamental question that can be easily overlooked is simply whether the metal in question is moving as an aqueous (water-based) molecular complex (that is as a single metal atom in solution surrounded by water molecules), as a metal oxide nanoparticle, or attached to an organic or inorganic particle or molecule. It is often assumed that if the metal in question passes a submicron filter (typically in the 0.2 to 0.5 micron range, i.e., 200 to 500 nm), then that metal is considered to be an aqueous species. In these cases, investigators simply have no better way to handle what is obviously missing from this approach. That is, metals can in fact, and presumably often are, transported within or on nanoparticles, not as aqueous species. Another layer of complexity can occur if a toxic metal is sorbed to a surface, but microbial interaction with that surface releases the metal. One of the lessons in this curriculum explores this possibility in some detail.



Nano2Earth Curriculum and the National Science Education Standards



Nano2Earth



4

The Nano2Earth curriculum provides students with the opportunity to learn about nanotechnology and nanoscience within the context of studying groundwater pollution through teaching science as inquiry. The curriculum is designed to meet the National Science Education Standards (NSES) for content in grades 9-12 (NRC, 1996). The following content standard categories are addressed in the curriculum: Unifying Science Concepts and Process, Science as Inquiry, Physical Science, Life Science, Earth Science, Science and Technology, Science in Personal and Social Perspectives, and History and Nature of Science. Each of these standards will be addressed in the context of the Nano2Earth curriculum design (see Appendix 1 for abbreviated description of NSES standards addressed in the Nano2Earth curriculum).

Unifying Concepts

The Nano2Earth is designed to assist students in making connections among the traditional scientific disciplines of biology, chemistry, earth science, and physics. For example, in the process of learning about groundwater pollution, students will explore the biogeochemistry of mineral-microbe interactions at the nanoscale. Within this context, students learn about the unifying concepts and processes as identified in the NSES (NRC, 1996, p. 113). The unifying concepts and processes include:

- Systems, order, and organization
- Evidence, models, and explanation
- Change, constancy, and measurement

- Evolution and equilibrium
- Form and function

Within the Nano2Earth curriculum, these concepts and processes include: (1) understanding the earth as an interconnected biological and physical *system* with different levels of complexity; (2) using *evidence* and mathematical modeling to interpret microbe-mineral interactions; (3) investigating *change* in biogeochemical systems under laboratory conditions; (4) using *measurement* and “scaling” from the macro to the nanoscale; and (5) examining how *form and function* apply to the interaction of bacteria with mineral surfaces.

Science as Inquiry

The Nano2Earth curriculum is designed to engage students in the process of conducting scientific inquiry. The pedagogy and teaching strategies are framed within the context of nanotechnology and nanoscience research on groundwater pollution. As outlined in the NSES (NRC, 1996, p. 175), the abilities to do scientific research include:

- Identify questions and concepts that guide scientific investigations
- Design and conduct scientific investigations

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Opposite page: Side view of an Atomic Force Microscope (AFM), a major tool in nanotechnology. André Green, shown loading the instrument, a former Chemistry teacher and current Ph.D. student in the Department of Teaching and Learning at Virginia Tech.

- Use technology and mathematics to improve investigations and communications
- Formulate and revise scientific explanations and models using logic and evidence
- Recognize and analyze alternative explanations and models
- Communicate and defend a scientific argument
- Understandings about scientific inquiry

Each lesson begins with an activity to engage students' prior knowledge by asking questions or brainstorming ideas about topics related to groundwater pollution and nanotechnology. Students actively participate in scientific investigations in the laboratory by exploring microbe-mineral interactions and

the transport of bacteria in groundwater, as simulated by the measurement of fluorescent beads transported through a sand column. Students learn how to use mathematical models to interpret and graph real scientific data that have been collected by atomic force microscopes. These microscopes are used to measure the nanoscale forces involved with microbe-mineral interactions. Students are also involved in web searches and investigating sources of groundwater pollution in their communities. As typical with "cutting edge" scientific research, students are encouraged to consider alternative explanations and models for explaining their data and what we know about microbe-mineral interactions.

Physical Science

Using nanotechnology and nanoscience, the Nano2Earth curriculum addresses the NSES in Physical Science.



Nano2Earth team member, Dr. Treavor Kendall, demonstrates to the Nano2Earth team how data from an Atomic Force Microscope can be converted to graphs known as force curves. Students will be asked to explore force curves in Lesson 5, "Nanoforces in Nature."

The NSES Physical Science standards addressed in the curriculum include the following categories for grades 9-12 (NRC, 1996, p. 176):

- Structure and Properties of Matter
- Chemical Reactions
- Motions and Forces

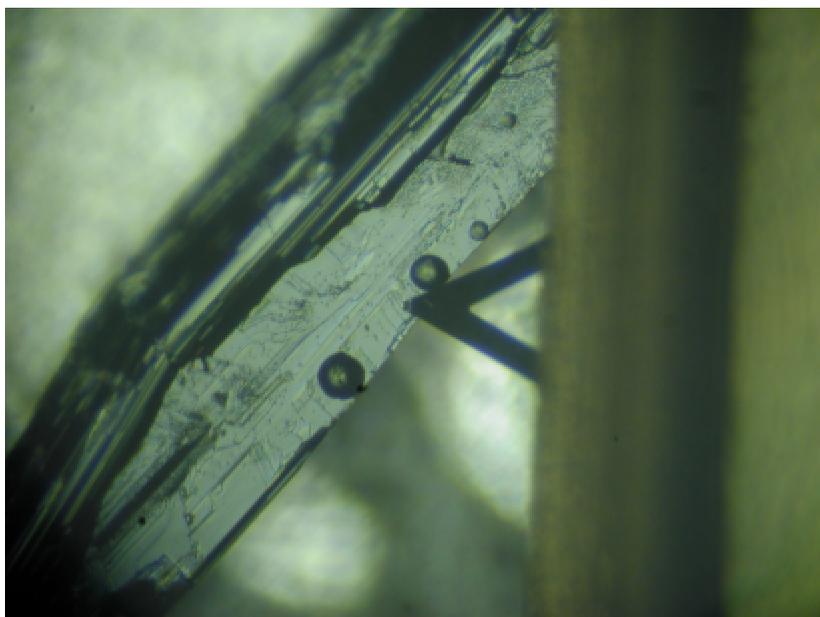
By examining images of mineral surfaces at the nanoscale, students learn about the structure of matter from new perspectives. As research has shown that nanoscale particles behave differently in the nanoscale than in the macroscale, students are exposed to new ways of thinking about the structure and interactions of matter. Students will investigate chemistry at the nanoscale by creating conditions in the laboratory to demonstrate the microbial reduction of iron (III). Students will then interpret data collected from atomic force microscopes that measure the forces (e.g., Van der Waals, electrostatic, hydrophobic) between bacteria and mineral surfaces which can be less than one nanoNewton.

Life Science

The national science standards addressed in Life Science include (NRC, p. 181):

- The Interdependence of Organisms
- Matter, Energy, and Organization of Living Systems
- Behavior of Organisms

By investigating the microbe-mineral interactions at the nanoscale, students will learn how matter and energy cycles and

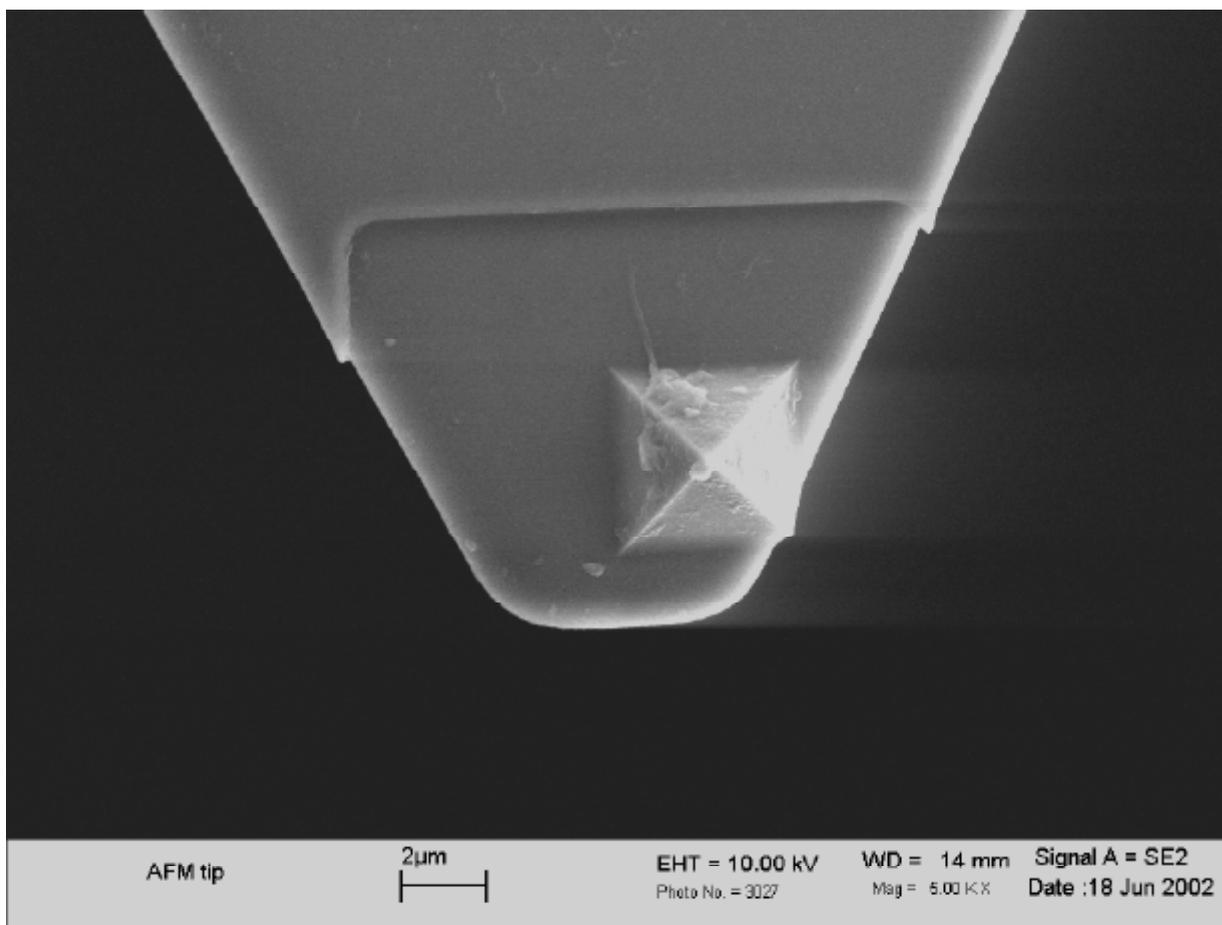


flows through different physical and biological systems. The adaptive response of bacteria to living in anaerobic conditions results in the extraction of iron (III) from mineral surfaces in the process of microbial respiration. Students will learn how groundwater pollution is influenced by the interaction of microbes and minerals.

Earth and Space Science

In support of the NSES in Earth Science, The Nano2Earth curriculum emphasizes an earth systems approach and specifically addresses the standard for learning about “Geochemical Cycles” (NRC, 1996, p. 189). Iron respiration of microbes is very important in geochemical cycling. In fact, microbes influence the distribution of many common elements on a global scale. Students will learn how microbe-mineral interactions are related to significant metal contamination (e.g., lead, chromium) and release of arsenic in the groundwater. Understanding microbe-mineral interactions in groundwater requires students to learn

This image of a cantilever in an Atomic Force Microscope (AFM) approaching a mineral surface was taken looking down the optics of the AFM. A sharp tip or other object (such as a bacteria-coated bead) is placed on the opposite side of the cantilever near the point of the V, such that it eventually comes in contact with the mineral.



This Scanning Electron Microscope image shows a pyramid-shaped tip from an Atomic Force Microscope cantilever. The tip was offset from the center during the manufacturing process. Notice the scale bar – the base of the tip is less than 3 microns (3,000 nm) across, and becomes much sharper near the top.

how geological, biological, and chemical systems interact.

Science and Technology

Students address the national standard for “Understanding about Science and Technology” by learning how science and our understanding of nature have advanced through the development of new technologies in nanoscience (NRC, 1996, p. 192). These new technologies include the atomic force microscope which measures forces between microbes and mineral surfaces at the nanoscale. In the Nano2Earth curriculum, students will learn how to interpret and make inference from data collected by this instrument. Research in nanotechnology and nanoscience requires the contributions of scientists from many disciplines, including engineering. Students will learn how

nanotechnology has contributed to our knowledge of groundwater pollution.

Science in Personal and Social Perspectives

Connecting science with personal and social perspectives is prominent in the NSES (NRC, 1996, p. 193). Specific standards addressed in the Nano2Earth curriculum include:

- Natural resources
- Environmental quality
- Natural and human induced hazards
- Science and technology in local, national, and global challenges

Groundwater pollution has enormous implications on the global scale for personal and community health. Waterborne diseases and metal and chemical contamination of groundwater dramatically affect the ability of the earth to sustain growing populations. Students will explore how the natural microbe-mineral systems adapt to changing environments, thus affecting water quality. As groundwater pollution can be induced naturally or by humans, it is important for students to learn how research in nanotechnology is advancing our understanding of these processes. The advancement of research in nanotechnology can lead to an assessment of cost, benefits, risks and possible solutions to groundwater pollution.

History and Nature of Science

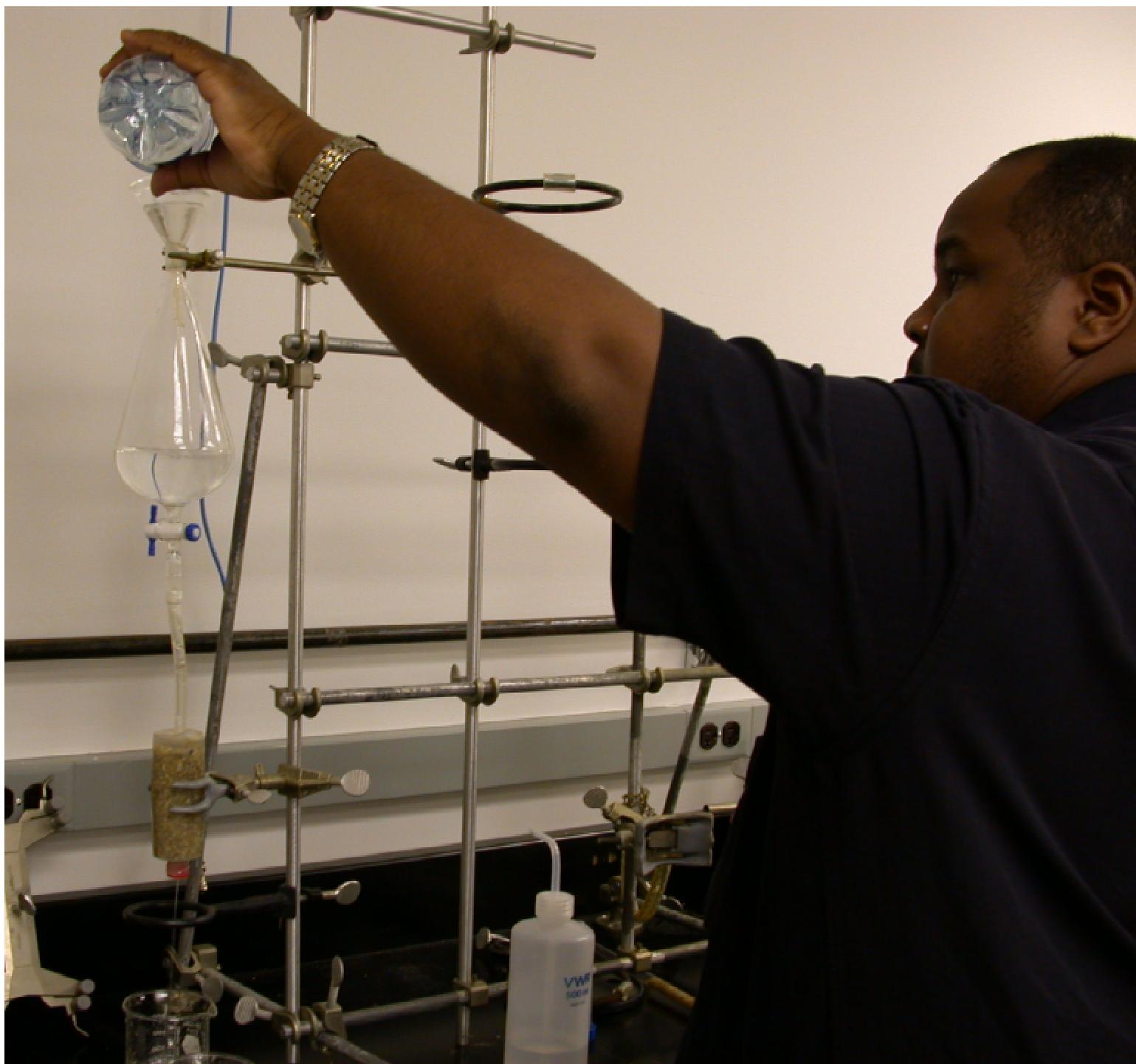
The Nano2Earth Project provides an excellent opportunity for students to learn about the nature of science and “cutting-edge” scientific research from a historical perspective. Research in science education and the National Science Education Standards have emphasized the importance of students’ understanding that science is a human endeavor in which:

- explanations of nature are formulated and tested using observational and experimental evidence;
- theoretical and mathematical models are used to interpret scientific data;
- science is tentative and subject to change; and
- scientific explanations are constructed and defended based on

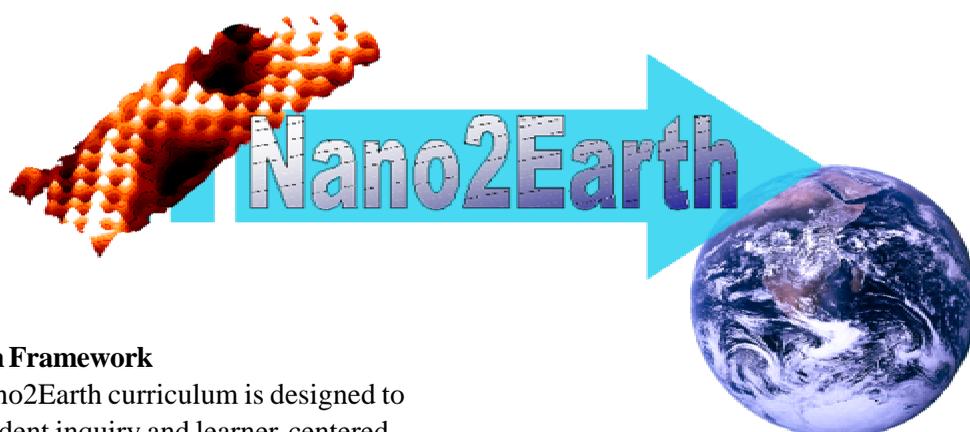
interpretation of evidence, experimental procedure, and theoretical explanations (NRC, 1996, p. 201).

Students will have the opportunity in the Nano2Earth Project to study the nature of scientific research by learning about the development of the field of nanotechnology and by exploring microbe-mineral interactions in groundwater. The activities will involve students with laboratory experiments in which they examine evidence of bacteria respiration of iron under anaerobic conditions and explore bacteria transport through porous substrate in groundwater. Using real scientific data from the laboratories of scientists in the Virginia Tech’s Department of Geosciences, students will analyze the nanoscale forces between bacteria and mineral surfaces through mathematical modeling and graphing. As the results are often tentative and subject to interpretation and careful analysis, students will learn about the “cutting-edge” nature of scientific research in nanotechnology.

National Research Council. 1996.
National Science Education
Standards. Washington, DC:
National Academy Press.



Nano2Earth Curriculum Overview



Curriculum Framework

The Nano2Earth curriculum is designed to promote student inquiry and learner-centered investigations of microbe-mineral interactions at the nanoscale. The curriculum is organized into five topics:

- *Lesson 1 – Introduction to Nanotechnology* is designed to introduce students to the nanotechnology through a scaling activity and a webquest of current events related to nanoscience research.
- *Lesson 2 – Introduction to Water Pollution* is designed to engage students in water testing and investigating groundwater pollution through know-wonder-learn charts and webquests.
- *Lesson 3 – Microbe-Mineral Interactions* involves students in a laboratory activity that promotes the reduction of iron (III) to iron (II) during the respiration of anaerobic bacteria by investigating interactions in a Winogradsky water column.
- *Lesson 4 – Investigation of Bacteria Transport in Groundwater* involves students in a probeware laboratory activity investigation designed to simulate the interactions of bacteria with mineral surfaces in a water column.
- *Lesson 5 – Nanoforces in Nature: Using Atomic Force Microscopy to Explore Mineral-Microbe Interactions* is designed for students to investigate nanoforces in nature by interpreting real scientific data

from microbe-mineral interactions. Students will also interpret simulated data of nanoforces involved in Winogradsky Column Lab (*Lesson 3*) and the Bacteria Transport Lab (*Lesson 4*).

The instruction and activities in each of the curriculum topics are designed to follow the 5-E Learning Cycle Model (Figure 1): Engage, Explore, Explain, Elaborate, and Evaluate (Bybee, 1993). This model is designed to “actively involve students in the inquiry process by accessing prior knowledge, utilizing strategies for scientific investigation of evidence, testing ideas, and reflecting on the results of investigations” (McLaughlin and Glasson, 2003, p. 49). The 5-E Learning Cycle Model has been promoted as an instructional model for teaching inquiry-based science (National Research Council, 2000).

How Do You Use The Curriculum?

The curriculum is designed to introduce students to nanoscale science and technology by investigating microbe-mineral interactions involved with groundwater pollution. Teachers may choose to use the entire curriculum or select topics that fit into their existing course. For example, science teachers who want to only introduce students to nanotechnology, may chose to complete Topic 1 (Introduction to Nanotechnology). Earth, life, or environmental science teachers may choose Topic 2 (Introduction to

Water Pollution) if their curriculum goals include the study of water pollution. Topic 3 (Microbe-Mineral Interactions) is ideal for chemistry classes in the study of microbial reduction of iron (III) but may also be selected by biology, earth or environmental science teachers for helping their students learn more about microbe-mineral interactions in anaerobic conditions and to highlight the differences between aerobic and anaerobic respiration. Topic 4 (Bacteria Transport in Groundwater) may be appropriate for chemistry and environmental science classes as it involves students in laboratory investigations that address particle transport and its affects on water quality. Teachers in all subjects may choose Lesson 5 (Atomic Force Microscope: Nanoforces in Nature) to apply nanotechnology to concepts from the previous lessons through the interpretation of real scientific data. Teachers may finish by having students complete one or both of the

scenarios with actual data that relate directly to the Winogradsky column or bacterial transport experiments. As the nanoscale science and technology is interdisciplinary in nature, the Nano2Earth curriculum also is inclusive of many scientific disciplines that are taught in secondary schools. Therefore, science teachers may choose to complete the entire curriculum to expose their students to the interdisciplinary nature of scientific research.

The Nano2Earth curriculum is designed to correlate with the National Science Education Standards (see Table 1, page 24). Each of the five lessons is designed to take 3-5 days to complete. A full description of the standards addressed in the Nano2Earth curriculum is provided in the Appendix (page 117).

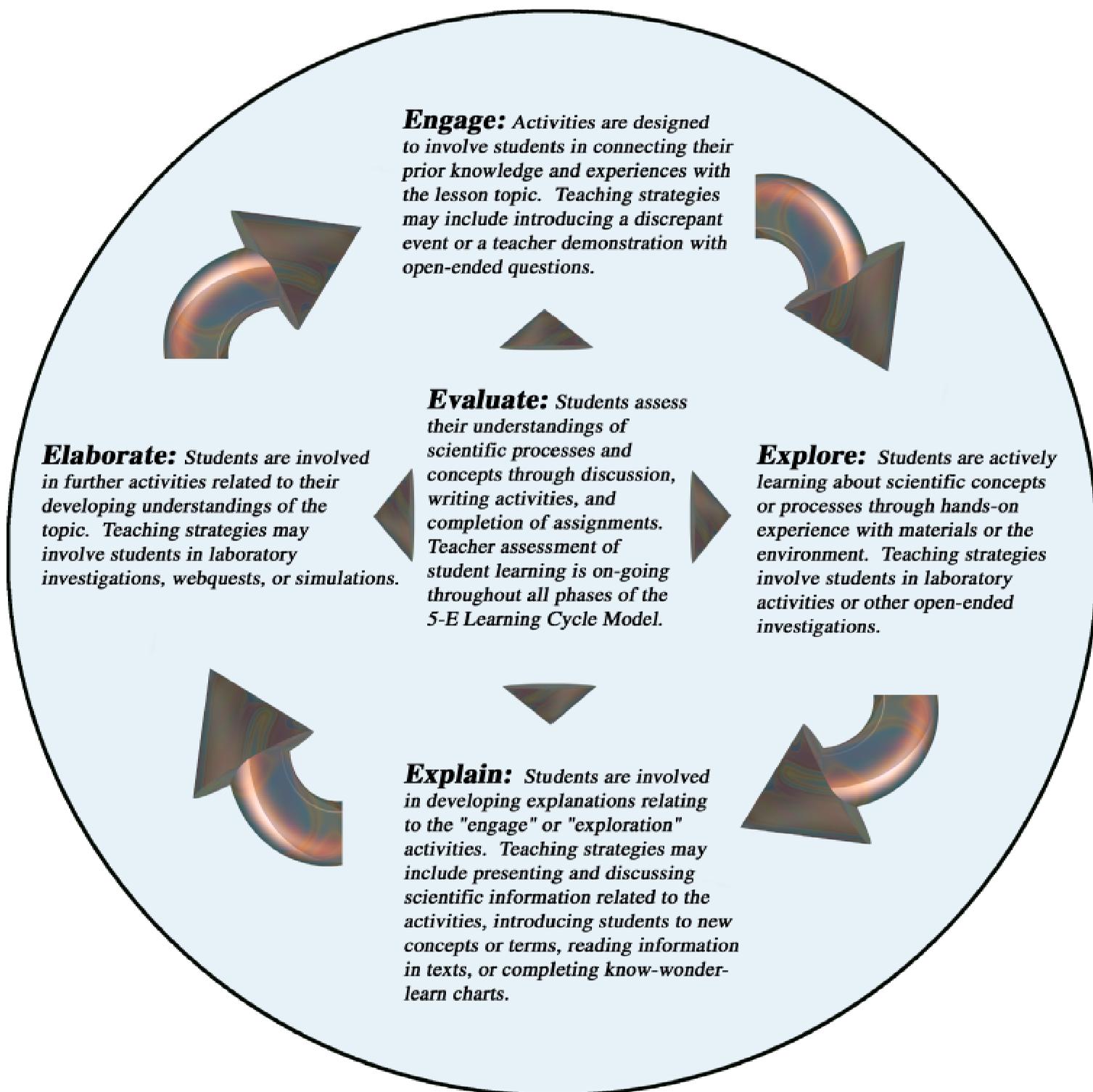


Figure 1: 5-E Learning Cycle Model

Table 1: Nano2Earth National Science Education Standards Lesson Correlation

Nano2Earth Lessons	NSES Standards Addressed
<p>1. <u>Introduction to Nanotechnology</u> Engage: Brainstorming Explore: Scaling Activity Explain: Why is the Nanoscale Important? Elaborate: Current Events Webquest Evaluate: Current Event Presentations</p>	<p>Unifying Concept</p> <ul style="list-style-type: none"> • Measurement <p>Science as Inquiry</p> <ul style="list-style-type: none"> • Using Technology and Mathematics to Improve Communications <p>Science and Technology</p> <ul style="list-style-type: none"> • Understanding about Science and Technology <p>Science in Personal and Social Perspectives</p> <ul style="list-style-type: none"> • Science and Technology in Local, National, and Global Challenges <p>History and Nature of Science</p> <ul style="list-style-type: none"> • Historical Perspectives
<p>2. <u>Introduction to Water Pollution</u> Engage: Teacher Demo – Glass of Water Explore: Water Testing Activity Explain: Water Pollution K-W-L Activity Elaborate: Water Pollution Webquest Activity Evaluate: K-W-L Chart & Writing Activity</p>	<p>Unifying Concepts</p> <ul style="list-style-type: none"> • Evidence • Explanations <p>Science as Inquiry</p> <ul style="list-style-type: none"> • Identify Questions and Concepts that Guide Scientific Explanations <p>Earth and Space Science</p> <ul style="list-style-type: none"> • Geochemical Cycles <p>Science in Personal and Social Perspectives</p> <ul style="list-style-type: none"> • Natural Resources • Environmental Quality • Natural and Human Induced Hazards • Science and Technology in Local, National, and Global Challenges

3. Mineral-Microbe Interactions

Engage: Prelab Questions

Explore: Winogradsky Column Lab

Explain: Discussion and Sharing of Results

Elaborate: Groundwater Scenario

Evaluate: Analysis and Conclusions

Unifying Concepts

- Systems
- Evidence
- Models
- Explanations
- Changes
- Measurement

Science as Inquiry

- Identify Questions and Concepts that Guide Scientific Explanations
- Design and Construct Scientific Investigations
- Using Technology and Mathematics to Improve Investigations and Communications
- Formulate and Revise Scientific Explanations and Models Using Logic and Evidence

Physical Science

- Structures and Properties of Matter
- Chemical Reactions

Life Science

- The Interdependence of Organisms
- Matter, Energy, and Organization of Living Systems

Earth and Space Science

- Geochemical Cycles

Science in Personal and Social Perspectives

- Environmental Quality
- Natural and Human Induced Hazards
- Science and Technology in Local, National, and Global Challenges

<p>4. Investigation of Bacterial Transport in Groundwater Engage: Groundwater Pollution Scenario and Waterborne Diseases Explore: Bacterial Transport in a Sand Column Explain: Class Discussion and Questions Elaborate: Influence of Groundwater Chemistry on Bacterial Transport Evaluate: Groundwater Pollution Scenario Revisited</p>	<p>Unifying Concepts</p> <ul style="list-style-type: none"> • Systems • Evidence • Models • Explanations • Changes • Measurement <p>Science as Inquiry</p> <ul style="list-style-type: none"> • Identify Questions and Concepts that Guide Scientific Explanations • Design and Conduct Scientific Investigations • Using Technology and Mathematics to Improve Investigations and Communications • Formulate and Revise Scientific Explanations and Models Using Logic and Evidence <p>Physical Science</p> <ul style="list-style-type: none"> • Structures and Properties of Matter • Motions and Forces <p>Earth and Space Science</p> <ul style="list-style-type: none"> • Geochemical Cycles <p>Science in Personal and Social Perspectives</p> <ul style="list-style-type: none"> • Environmental Quality • Natural and Human Induced Hazards • Science and Technology in Local, National, and Global Challenges
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5. Nanoforces in Nature

Engage: The Atomic Force Microscope (AFM)

Explore: Bacteria and Minerals Together with the AFM

Explain: Force Curve Computer Simulations

Elaborate: Building a Model AFM

Evaluate: Scenario

Unifying Concepts

- Systems
- Evidence
- Models
- Explanations
- Changes
- Measurement
- Form and Function

Science as Inquiry

- Identify Questions and Concepts that Guide Explanations
- Design and Conduct Scientific Investigations
- Using Technology and Mathematics to Improve Investigations and Communications
- Formulate and Revise Scientific Explanations and Models Using Logic and Evidence
- Recognize and Analyze Alternative Explanations and Models
- Understanding About Scientific Inquiry

Physical Science

- Structures and Properties of Matter
- Motions and Forces

Earth and Space Science

- Geochemical Cycles

Science and Technology

- Understanding About Science and Technology

Science in Personal and Social Perspectives

- Natural Resources
- Environmental Quality
- Natural and Human Induced Hazards
- Science and Technology in Local, National, and Global Challenges History and Nature of Science
- Science as a Human Endeavor
- Nature of Scientific Knowledge
- Historical Perspectives

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These flasks contain suspensions of nano-sized CdSe particles known as “quantum dots”. The color arises after UV illumination. The only difference between the flasks are the size of the particles, ranging from 2 nm (left) to approximately 5 nm (right).

Lesson 1

Introduction to Nanotechnology

Purpose

The purpose of Lesson 1 is to identify and compare the scale of different objects, define the nanoscale and nanoscience, and introduce history and applications of nanoscience.

Background Information

Imagining differences in scale can be very easy (a softball is bigger than a baseball) or very difficult (how can we imagine the size of a galaxy?). It is perhaps most challenging to build conceptual frameworks for objects that are too small to see. In fact, the world of inner space is more vast and daunting to the imagination than the entire world visible to us on Earth and the nearby solar system. Nanoscience is the field of science that measures and explains the changes of the properties of substances as a function of size; these changes occur in the range of approximately 1-100 nm. Nanotechnology simply takes advantage of this phenomenon by applying property modifications of this nature to some beneficial endeavor. Chapters 1-3 of the Nano2Earth book provide a descriptive background to nanoscience, nanotechnology, and their roles in Earth and environmental science designed for the teacher.

National Standards

Nano2Earth Lessons	NSES Standards Addressed
<p>Introduction to Nanotechnology</p> <p>Engage: Brainstorming</p> <p>Explore: Scaling Activity</p> <p>Explain: Why is the Nanoscale Important?</p> <p>Elaborate: Current Events Webquest</p> <p>Evaluate: Current Event Presentations</p>	<p>Unifying Concept</p> <ul style="list-style-type: none"> • Measurement <p>Science as Inquiry</p> <ul style="list-style-type: none"> • Using Technology and Mathematics to Improve Communications <p>Science and Technology</p> <ul style="list-style-type: none"> • Understanding about Science and Technology <p>Science in Personal and Social Perspectives</p> <ul style="list-style-type: none"> • Science and Technology in Local, National, and Global Challenges <p>History and Nature of Science</p> <ul style="list-style-type: none"> • Historical Perspectives

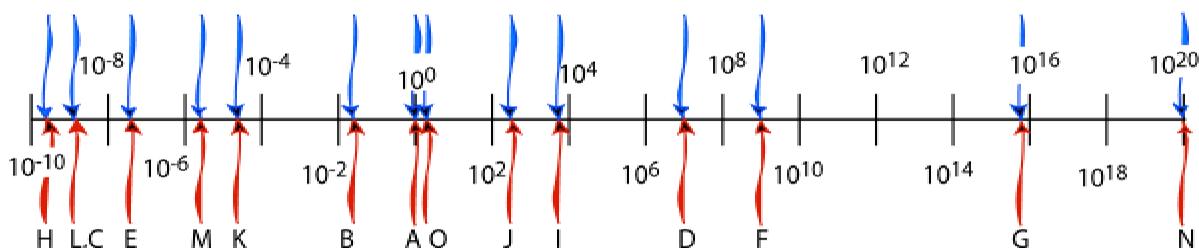
Engage: Brainstorming

The class will brainstorm to identify and compare the scale of different objects. On a piece of paper or chalkboard, make a list of the largest objects you can see and the smallest objects you can see. Rank the objects according to estimated size. Ask the student to add objects to the list that can be seen only see with scientific instruments (e.g., telescope, microscope). Discuss how you would compare the size of these objects.

Explore: Scaling Activity

- Key points to review of units and scientific notation
 - 1 meter = the System International (SI) standard unit of length. All length scales are referenced to this length.
 - Scientific notation is related to “orders of magnitude”...numbers multiplied by powers of ten.
 - Multiply 1 meter by 10, which gives a decimeter, or 1×10^1 meters. Multiply 1 meter by 1000, that gives a kilometer, or 1×10^3 meters ($1 \text{ m} \times 10 \times 10 \times 10 = 1000 \text{ m}$).
 - Multiply 1 meter by 0.001 = millimeter or 1×10^{-3}
- Introduce the term *nanometer* (nm) or 1×10^{-9} or a billionth of a meter. The *nanoscale* is considered 1-100 nm.
- Instruct students to complete the activity “The Scale of the Earth Sciences” by placing the letter corresponding to each object on the scale above the appropriate arrow. The upper set of arrows is for the students’ estimations, while the lower set of arrows is for the students to write down the answers given by the teacher.
- When students are finished, give them the correct answers from the list below and have them complete the scale of the actual size of the objects (write in underneath the lower set of arrows). Note that both L and C are associated with the same arrow.

H. Diameter of an atom	1×10^{-10} to 5×10^{-10} m
L. A nanometer	1×10^{-9} m
C. Diameter of a DNA	1×10^{-9} m
E. Diameter of a typical virus	1.5×10^{-8} to 5×10^{-7} m
M. Diameter of typical bacteria	0.2×10^{-6} to 2×10^{-6} m
K. The width of a human hair	6×10^{-5} m
B. The length of your thumbnail	2×10^{-2} m
A. A meter	1 m
O. Your height	1.7 m
J. Height of the Empire State Building	4.48×10^2 m
I. Height of Mount Everest	8.848×10^3 m
D. Diameter of the Earth	1.27×10^7 m
F. Diameter of the Sun	1.39×10^9 m
G. A light year	9.5×10^{15} m
N. Distance across Milky Way Galaxy	10^{20} m

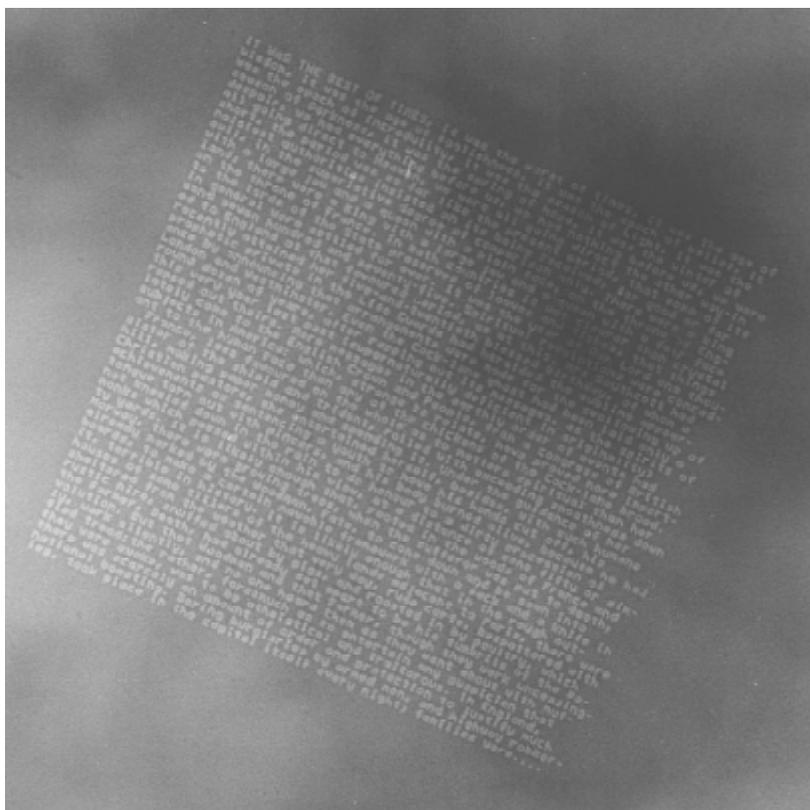


5. Instruct the students to answer the summary questions and then review the correct answers.
- Which part of the scale is considered the nanoscale?
1- 100 nm
 - What is the smallest part of the scale that your eye can see?
About 10^{-5}
 - What is the smallest part of the scale that a classroom microscope can see?
About 10^{-6}
 - On the scale, is your height closer to Mount Everest or to a nanometer?
Mount Everest
 - What distance separates 10^0 and 10^2 ? What distance separates 10^2 and 10^4 ? Notice that your answers should not be the same.
99 m 99001 m

Explain: Why is the Nanoscale Important?

1. Have the students read the activity sheet “There’s Plenty of Room at the Bottom”. It contains excerpts from the lecture of the same name given by the physicist Richard Feynman at CalTech in 1959. It was first published in the February 1960 issue of Caltech’s *Engineering and Science*, and at the time of this writing, the entire speech could be found online at <http://www.its.caltech.edu/%7Efeynman/>.
2. Tell the students that at the end of the lecture, Dr. Feynman announced a \$1,000 prize for the first people to make an electric motor only $1/64^{\text{th}}$ inch cubed and another \$1,000 for the first person to write a passage from a book at $1/125,000$ smaller scale than the original text. Do the students think these have been accomplished, and when?

The two Feynman Prizes mentioned in the lecture were awarded in 1960 (making a $1/64^{\text{th}}$ inch operating electric motor) and in 1985 (minimizing a page of a book at $1/125,000^{\text{th}}$ scale so it could be clearly interpreted by an electron microscope). The prize-winning Transmission Electron Micrograph, taken by Drs. Pease and Newman from Stanford in 1985 is shown here.



1. Introduction to Nanotechnology

3. Ask the students if they think it is currently possible to image and manipulate atoms.

The answer is yes! Using a tool called the Scanning Tunneling Microscope (STM), which the students will learn more about in Lesson 5, it is possible to both image and manipulate individual atoms of certain types.

4. If it is possible to view and move individual atoms, why can't we build anything we want? If sources of the necessary atoms were available, why can't they just be organized in the arrangement of any material? These very questions are at the heart of current debate in nanotechnology. One of the original proponents of these ideas, Eric Drexler, considers this to be the future of nanotechnology. Known by Dr. Drexler as "molecular manufacturing" or "molecular nanotechnology", the possibility of creating nearly anything from constituent atoms may revolutionize human society. However, many scientists including Dr. Richard Smalley suggest that such synthesis is not possible. Dr. Smalley was awarded a Nobel Prize in Chemistry for his work in the discovery of carbon nanostructures. He and others suggest that bringing atoms in proximity to one another is not enough to cause the necessary bonding arrangements to occur in the resulting molecules. Present your students with the idea of building materials from 'scratch'. What thoughts do they have for and against this idea?

Elaborate: Current Events Webquest

Assign students to find a current event on nanoscience. This can be done as a homework assignment or in the computer lab over the internet. Instruct students to seek recent articles in the newspaper, magazines, or on the web dealing with new technologies, applications, or products that are developed using nanotechnology. Links to nanoscale science and technology can be found on this website: <http://www.nanoed.vt.edu/links.htm>.

Evaluate: Current Event Presentations

Students can summarize and present current events for assessment of their understanding of nanoscale sizes and potential applications of nanotechnology. Students should: be able to (1) describe the new technology, application, or products; (2) identify the size or scale of the objects or products; and (3) discuss the potential use of the new technologies, applications, or products to society.

Introduction to Nanotechnology

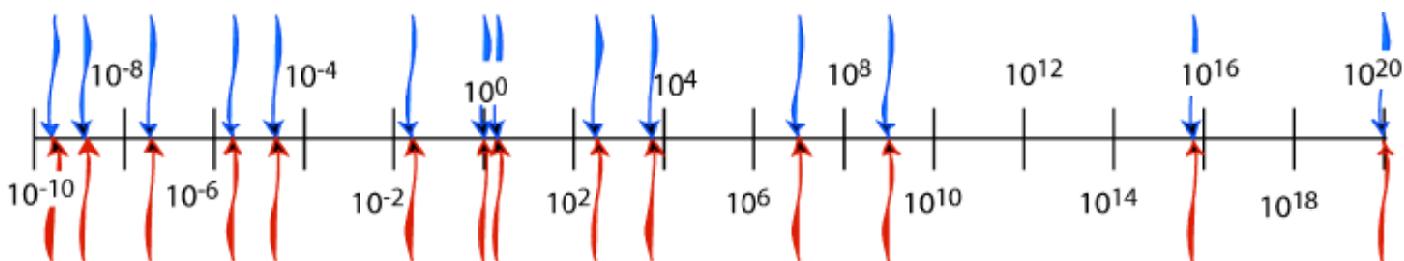
Nano2Earth Activity Sheet

The Scale of the Earth Sciences Activity

On your worksheet, you see a scale showing a wide range of measurements, from extremely small to extremely large. Below is a list of objects from all areas of the scale. Estimate the size of each object, and place the corresponding letter on the scale above the arrows. Afterward, your teacher will provide the answers for you to write below the bottom set of arrows. The scale is in meters.

- A meter
- | | |
|---------------------------------|---|
| A. The length of your thumbnail | I. Height of Mount Everest |
| B. Diameter of a DNA | J. Height of the Empire State Building |
| C. Diameter of the Earth | K. The width of a human hair |
| D. Diameter of a typical virus | L. A nanometer |
| E. Diameter of the Sun | M. Diameter of typical bacteria |
| F. A light year | N. Distance across the Milky Way Galaxy |
| G. Diameter of an atom | O. Your height |
| H. | |

Estimated size



Actual size

Summary Questions

Answer the following summary questions:

- Which part of the scale is considered the nanoscale?
- What is the smallest part of the scale that your eye can see?
- What is the smallest part of the scale that a classroom microscope can see?
- On the scale, is your height closer to Mount Everest or to a nanometer?
- What distance separates 10^0 and 10^2 ? What distance separates 10^2 and 10^4 ? Notice that your answers should not be the same.

Introduction to Nanotechnology

Nano2Earth Activity Sheet

“There’s Plenty of Room at the Bottom” Activity

Excerpts from: Plenty of Room at the Bottom
Richard P. Feynman
December 1959 Lecture in the Department of Physics at CalTech

I would like to describe a field, in which little has been done, but in which an enormous amount can be done in principle... a point that is most important is that it would have an enormous number of technical applications.

What I want to talk about is the problem of manipulating and controlling things on a small scale.

As soon as I mention this, people tell me about miniaturization, and how far it has progressed today. They tell me about electric motors that are the size of the nail on your small finger. And there is a device on the market, they tell me, by which you can write the Lord’s Prayer on the head of a pin. But that’s nothing; that’s the most primitive, halting step in the direction I intend to discuss. It is a staggeringly small world that is below. In the year 2000, when they look back at this age, they will wonder why it was not until the year 1960 that anybody began seriously to move in this direction.

Why cannot we write the entire 24 volumes of the Encyclopaedia Britannica on the head of a pin?

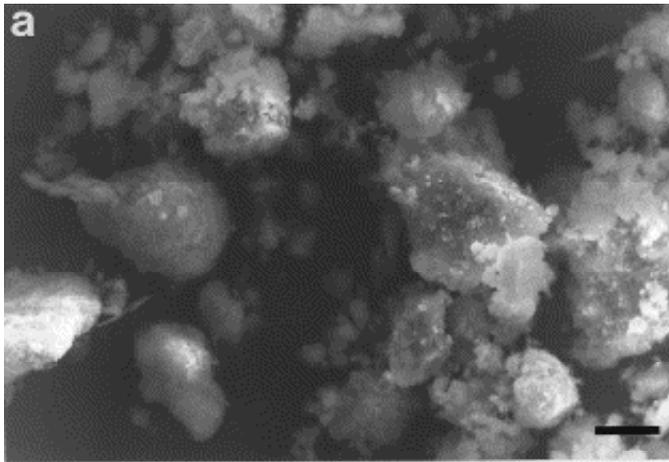
Let’s see what would be involved. The head of a pin is a sixteenth of an inch across. If you magnify it by 25,000 diameters, the area of the head of the pin is then equal to the area of all the pages of the Encyclopaedia Britannica. Therefore, all it is necessary to do is to reduce in size all the writing in the Encyclopaedia by 25,000 times. Is that possible? The resolving power of the eye is about 1/120 of an inch—that is roughly the diameter of one of the little dots on the fine half-tone reproductions in the Encyclopaedia. This, when you demagnify it by 25,000 times, is still 80 angstroms in diameter—32 atoms across, in an ordinary metal. In other words, one of those dots still would contain in its area 1,000 atoms. So, each dot can easily be adjusted in size as required by the photoengraving, and there is

no question that there is enough room on the head of a pin to put all of the Encyclopaedia Britannica. ...

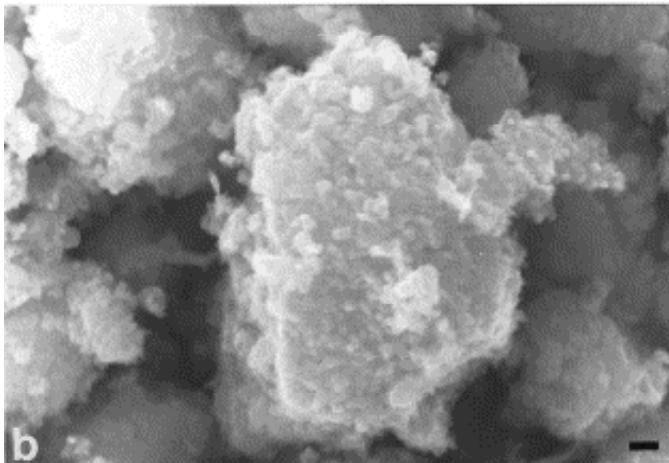
That’s the Encyclopaedia Britannica on the head of a pin, but let’s consider all the books in the world. The Library of Congress has approximately 9 million volumes; the British Museum Library has 5 million volumes; there are also 5 million volumes in the National Library in France. Undoubtedly there are duplications, so let us say that there are some 24 million volumes of interest in the world.

What would happen if I print all this down at the scale we have been discussing? How much space would it take? It would take, of course, the area of about a million pinheads because, instead of there being just the 24 volumes of the Encyclopaedia, there are 24 million volumes. The million pinheads can be put in a square of a thousand pins on a side, or an area of about 3 square yards...all of the information which all of mankind has every recorded in books can be carried around in a pamphlet in your hand—and not written in code, but a simple reproduction of the original pictures, engravings, and everything else on a small scale without loss of resolution.

What would our librarian at Caltech say, as she runs all over from one building to another, if I tell her that, ten years from now, all of the information that she is struggling to keep track of— 120,000 volumes, stacked from the floor to the ceiling, drawers full of cards, storage rooms full of the older books—can be kept on just one library card! When the University of Brazil, for example, finds that their library is burned, we can send them a copy of every book in our library by striking off a copy from the master plate in a few hours and mailing it in an envelope no bigger or heavier than any other ordinary air mail letter.



Scanning Electron Microscope (SEM) image of sediments from a contaminated river. The black bar is 10 micrometers (10,000 nm) on the top image and 1 micrometer (1,000 nm) on the bottom image



At the nanoscale, other more powerful techniques such as Transmission Electron Microscopy (TEM) reveal the true story of the sediment. Here the black scale bar is 100 nm - many of the features in the image are less than 10 nm! The box inset to the lower left is a diffraction pattern, used to identify minerals.



Lesson 2

Introduction to Water Pollution

Purpose

The purpose of this lesson is to assess students' prior knowledge about groundwater pollution and let students investigate types and sources of water pollution. Note that this introductory activity sets the stage for subsequent learning about sources of water pollution.

Background Information

Find out the source of your water—groundwater, a local river or stream, a spring, a reservoir. No matter what the source, it probably contains some or all of the following contaminants. Microbial contaminants include *E. coli*, *Cryptosporidium*, *Giardia*, and *Salmonella*. Chemical contaminants include arsenic, pesticides, radon, lead, and nitrates. These contaminants may originate from both natural and manmade sources such as industry, agriculture, and local geology.

In these activities, students work both individually and in small groups to analyze and present information about water pollution to the class.

The Environmental Protection Agency (EPA) sets maximum contamination levels (MCL's) for water sources. A list of these along with the specific problems they cause for humans can be found at the EPA website, <http://www.epa.gov/safewater/mcl.html#mcls>. A list is also included as a student activity sheet in the elaboration phase.

National Standards

Nano2Earth Lessons	NSES Standards Addressed
<p>Introduction to Water Pollution</p> <p>Engage: Teacher Demo – Glass of Water</p> <p>Explore: Water Testing Activity</p> <p>Explain: Water Pollution K-W-L Activity</p> <p>Elaborate: Water Pollution Webquest Activity</p> <p>Evaluate: K-W-L Chart & Writing Activity</p>	<p>Unifying Concepts</p> <ul style="list-style-type: none"> • Evidence • Explanations <p>Science as Inquiry</p> <ul style="list-style-type: none"> • Identify Questions and Concepts that Guide Scientific Explanations <p>Earth and Space Science</p> <ul style="list-style-type: none"> • Geochemical Cycles <p>Science in Personal and Social Perspectives</p> <ul style="list-style-type: none"> • Natural Resources • Environmental Quality • Natural and Human Induced Hazards • Science and Technology in Local, National, and Global Challenges

2. Introduction to Water Pollution

Materials

- Four beakers
- Tap water
- Bottled water
- Rainwater
- River/lake water
- Water quality test kits (available from Watersafe @ www.watersafetestkits.com for \$16.99)
- Either class set of internet-ready computers or information sheets provided
- Student Activity Sheets

Engage: Teacher Demo - Glass of Water (Estimated time: 10 minutes)

Display a beaker of tap water, a beaker of bottled water, a beaker of rainwater, and a beaker of river or lake water in the front of the room. Do not tell students which beaker contains which water sample. Simply label the beakers 1, 2, 3, and 4. Tell the students that each of the beakers holds water from a different source. Ask students the following questions about each of the beakers:

- Does this water look clean to you?
- Would you drink this water? Why or why not?
- What do you think was the source of this water?
- What might be in this water? What evidence do you have for this?
- How could we find out what is in this water?

Encourage the students to smell the water. Do not let the students drink the water.

Explore: Water Testing Activity (Estimated time: 30 minutes)

1. Pass out student activity sheets. Instruct students to make an hypothesis about where each water sample originated.
2. Break students into groups. Assign each group one of the water quality tests—bacteria, lead, pesticides, nitrates, nitrites, chlorine, pH, and hardness. Give each group a small container of each of the water samples 1-4 and the appropriate test kit.
3. Science Safety: Students should not ingest water samples. Students should wear goggles when using water quality test kits. Note that bottled water may also contain contaminants.
4. Instruct each group to circle the test they are performing on the activity sheet.
5. Instruct each group to test the four water samples and record their data on the sheet provided.
6. When testing is complete, tell one person from each group to record their data on the board.
7. Direct students to copy the class data from the board.
8. Direct students to answer questions on the activity sheet.

Explain: Water Pollution K-W-L Activity (Estimated time: 15 minutes)

Know-Wonder-Learn (K-W-L) charts provide a means to outline what students already know about a topic, to explore what they want to learn about it, and, perhaps most importantly, to track their own learning throughout a unit. Although they can be used on their own, K-W-L charts can be especially effective when used in conjunction with periodic reflections throughout a unit. We encourage you to try one or both techniques as you lead your students through these lessons.

K-W-L charts can be constructed individually or you may want to make one chart for the whole class and begin to fill it in as part of a class discussion. Students construct their chart at the beginning of the lesson, after the Engage activity. They should be able to fill in some boxes in the first column and perhaps some in the second column as well. After this initial construction, the class can revisit the chart every few days to fill in more. If students find that their statements of prior knowledge were incorrect, they can revise them in the third column. K-W-L charts are about the learning process; they are not about being right!

Below is a sample of a K-W-L chart for “Water Pollution”. A blank chart is included as a student activity sheet.

What do I know about water pollution?	What do I wonder about water pollution?	What have I learned about water pollution?
Fertilizer runoff hurts the water	Is there a type of fertilizer that doesn't hurt the water?	Fertilizer-laden runoff causes algal bloom and eutrophication in farm ponds
Arsenic in water may be poisonous	What is the source of the arsenic? Is there arsenic in my water? Am I being poisoned?	
What does water pollution have to do with nanoscience?		

If students work on these individually, you can collect and grade their K-W-L charts periodically to help gauge student progress throughout the unit. Things to consider when grading these products of students' learning include: depth of student thinking and student growth from beginning to end of unit.

Elaborate: Water Pollution Webquest Activity (Estimated time: 30 minutes)

In this activity, students will complete a webquest to find information about water pollution in their community. This activity is best if you have access to a class set of computers. Otherwise, you may print out information from the websites for students to find the answers to the questions. The websites that are included were current at the time of publication, but should be checked and updated if necessary. You will have to do some research to find the source of your local water. The EPA website listed in the activity sheet includes information on local water sources and quality for many areas in the United States.

2. Introduction to Water Pollution

Many of the contaminants listed below occur as a result of “erosion of natural deposits”. The following table lists a few of the minerals in which each of the contaminants occurs.

Contaminant	Source
Arsenic	Arsenopyrite (FeAsS) Realgar (AsS) Orpiment (As_2S_3)
Asbestos	Group of fibrous aluminosilicate minerals
Barium	Contact with sedimentary rocks, mainly carbonates (limestone / dolomite) and evaporites (rock gypsum)
Cadmium	Greenockite (CdS)
Chromium	Chromite (Cr_3O_4)
Copper	Chalcopyrite (CuFeS_2)
Fluoride	Fluorite
Lead	Galena (PbS) Cerussite (PbCO_3) Pyrite (FeS_2)
Mercury	Cinnabar (HgS)
Nitrate and nitrite	Nitrogen occurs in soil in organic farms from decaying plant and animal residues; converted to nitrate by bacteria in soil
Radium	Contact with granitic rocks
Selenium	Trace element in coal deposits
Uranium	Zircon (ZrSiO_4) Uraninite (UO_2)

Evaluate: K-W-L Chart and Writing Activity (Estimated time: 30 minutes)

In the last section, students will synthesize what they have learned about water contamination so far by writing a response to the question given on the activity sheet.

Introduction to Water Pollution

Nano2Earth Activity Sheet

Water Testing Activity

Hypothesis

Each of the four samples comes from a different source. What do you think is the source of each of the four water samples: tap water, bottled water, stream/lake water, or rainwater? Explain why you think each sample originates where it does. Record your answers below.

Science Safety: Students should not ingest water samples. Students should wear goggles when using water quality test kits. Note that bottled water may also contain contaminants.

Sample 1 Source: _____ *Sample 3* Source: _____
 Reason: _____ Reason: _____

Sample 2 Source: _____ *Sample 4* Source: _____
 Reason: _____ Reason: _____

	Sample 1	Sample 2	Sample 3	Sample 4
Bacteria				
Lead				
Pesticides				
Nitrates				
Nitrites				
Chlorine				
pH				
Hardness				

Questions:

1. Considering the test results, where do you think each of the water samples originates? Explain your answers.

2. Show this sheet to your teacher. She will tell you the actual source of each sample. Compare the actual sources to your revised hypothesis in question 1. Based on the test results, which water seems “cleanest”?

3. Look at any contaminants that occurred in the samples you tested. Considering where each sample originates, what do you think is the contaminant source of each one?

Introduction to Water Pollution
Nano2Earth Activity Sheet

Water Pollution Know-Wonder-Learn (K-W-L) Activity

What do I know about water pollution?	What do I wonder about water pollution?	What have I learned about water pollution?

Introduction to Water Pollution Nano2Earth Activity Sheet

Water Pollution Webquest Activity (Your Community)

Directions: Use the websites below to find information about water quality in your community.

Helpful Websites for information about water pollution

The EPA website— <http://www.epa.gov/safewater/mcl.html#mcls>

This site includes regulations involving drinking water, lists of contaminants and their maximum levels, and potential health effects from contaminants.

Local drinking water— <http://www.epa.gov/safewater/dwinfo.htm>

The EPA provides state-by-state information on drinking water sources and drinking water quality.

Water use, water sources, water pollution— <http://ga.water.usgs.gov/edu/mwater.html>

The USGS provides information on water use, water sources, water contamination, and what people are doing to prevent it. Includes information on how contaminants leak into groundwater and on how storm sewers work.

How Stuff Works Website— <http://people.howstuffworks.com/sewer.htm>

This site describes what happens to your wastewater—where it goes and how it becomes clean again.

1. Drinking water comes from many sources—rivers, lakes/reservoirs, springs, groundwater, and cisterns. Some localities even use desalinated seawater.
 - What is the source of your drinking water?
 - If you get city or county water, how much does it cost?
 - How is it treated before it is piped to your house?
 - What do the treatments eliminate or add to the water?
2. Once water has been used, it may take one of many paths back into the local water supply.
 - What is the source of the water in a storm drain? How is this water treated before it drains back into the water supply?
 - What is the source of the water in a sewer pipe? How is this water treated before it drains back into the water supply?
 - What happens to the water that goes down the drain at your home or school?
 - What happens to the water that falls onto your roof when it rains?
3. Farmers and homeowners use many types of pesticides, herbicides, and fertilizers on their lawns and fields.
 - How do these contaminants end up in the water supply?
 - How long does it take for such contaminants to get into the groundwater?

Introduction to Water Pollution Nano2Earth Activity Sheet

4. If your drinking water comes from a municipal source, then it must meet federal and state guidelines for safe drinking water. If it comes from a well or a spring, it is up to you to test it.
- What federal agency regulates drinking water in the United States? What do the abbreviations “ppm” and “mg/L” represent?
 - What is the difference between “MCL” and “MCLG”?
 - Notice that the EPA divides contaminants into six categories: Microorganisms, Disinfectants, Disinfection Byproducts, Inorganic Chemicals, Organic Chemicals, and Radionuclides. Notice that the sources of these contaminants vary widely. Some are naturally occurring, some are manmade, and some are both. The types of contaminants in your water depend upon where you live. For each of these categories, find one contaminant that might occur in **your** water. Write the name of the contaminant, its source, the category it belongs to, and the potential health effects from ingestion of water that contains this contaminant. Organize your answers in a table like the one below:

Category	Contaminant	Source	Potential Health Effects
Microorganisms			
Disinfectants			
Disinfection byproducts			
Inorganic chemicals			
Organic chemicals			
Radionuclides			

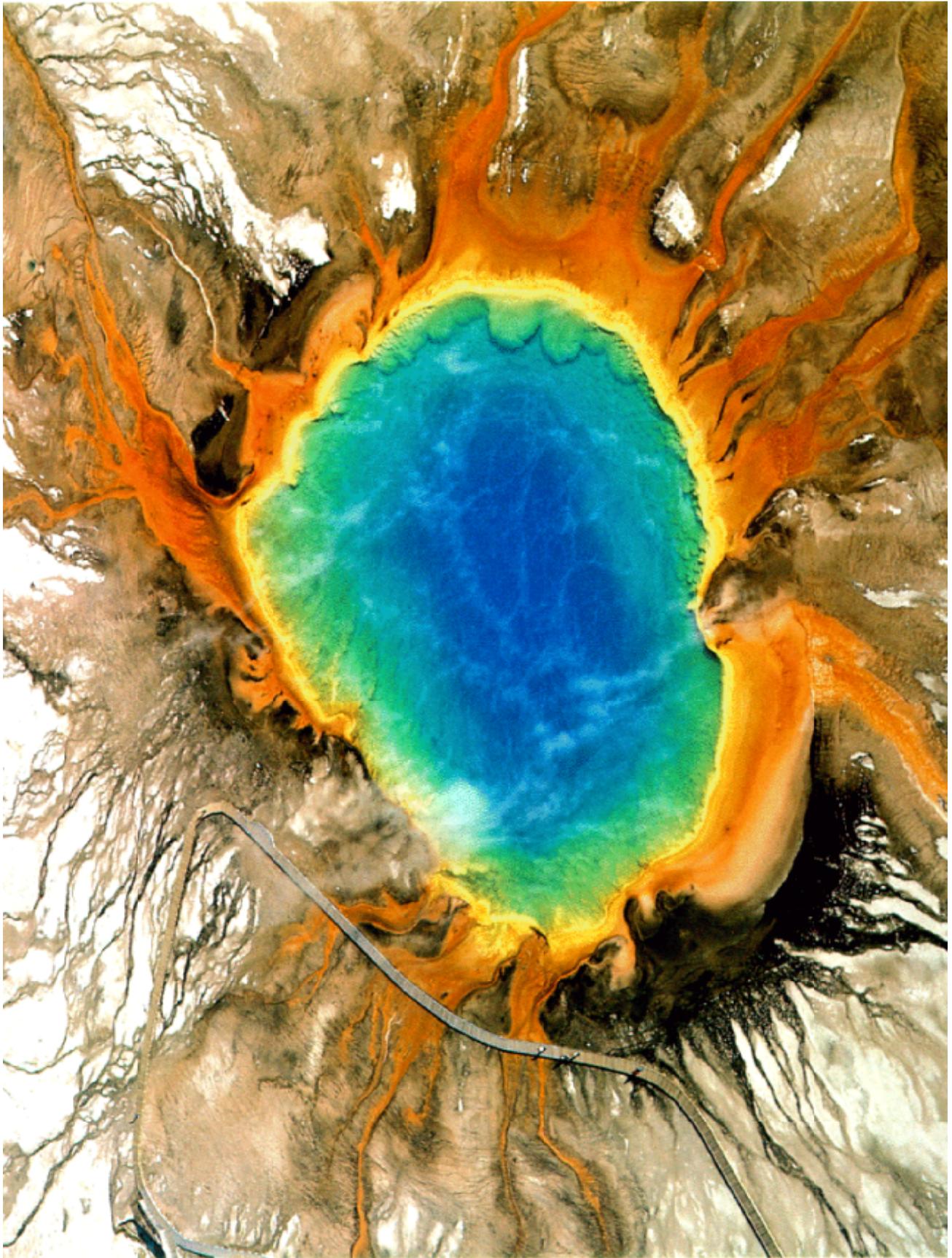
Introduction to Water Pollution Nano2Earth Activity Sheet

K-W-L Written Response Activity

Synthesize what you have learned and compose a written response to the following question:

Over 1 billion people worldwide—almost one-sixth of the world population—lack access to safe drinking water and over 2 billion people lack basic sanitation facilities. In some countries in Africa and Asia, many children do not go to school because they must spend their time collecting water for their families. According to WaterAid, a child dies every 15 seconds due to water-related diseases. It is hard for most Americans to imagine living without clean drinking water and a place to go to the bathroom. Yet even in America, over 7 million people become sick from contaminated drinking water each year.

As the population of an area grows, the water supply becomes an increasing concern. Pretend you are a scientist that has been asked to give a presentation to the local Board of Supervisors. Given what you have learned about water quality and the water supply of your area, write a short speech to be delivered to the Board. Include a summary of the results of your water quality testing, any concerns the contaminants present for the community, and your recommendations for improving or maintaining the quality of your water supply. Your speech should be a minimum of two minutes long and may certainly be longer. Be sure to support your ideas with the data you have collected both experimentally and from the Web.



Different colors in the Grand Prismatic hot spring of Yellowstone National Park are due to microbes that survive by using chemicals from the hot spring water.

Lesson 3

Microbe-Mineral Interactions: Using the Winogradsky Column to Demonstrate Microbial Reduction of Fe(III)

Purpose

The purpose of this investigation is for students to study the reduction of iron oxide minerals in a simulated anaerobic aquatic environment. Students will discuss how the respiration of anaerobic bacteria may be involved with iron reduction. Students will also consider problems related to excessive nutrients entering surface waters and what role students can play to help sustain the health of the earth's waters.

Background Information

The overarching goal of this experiment is to join the sciences—Earth Science, Biology, and Chemistry—in order to examine a process that is most likely unfamiliar to the students, the microbial reduction of Fe^{3+} to Fe^{2+} . Unfortunately, it is impossible for students to directly witness the role of nanoscale interactions during any experiment, but students will learn in Lesson 5 about how nanoscale interactions promote the reduction of the iron (III) to iron (II) during the respiration of the anaerobic bacteria. Students most likely will have some limited prior knowledge about water, water quality, bacteria, and respiration when beginning the lab, so the lab provides an opportunity for strengthening the student's knowledge and understanding of these concepts.

The experiment also provides an opportunity to use probeware, so that the students can begin to feel comfortable with this type of technology.

If the students are currently enrolled in a biology course or have had a biology course, they may be familiar with aerobic respiration, the complicated process by which organisms take up oxygen and produce carbon dioxide and water. Bacteria get energy from this reaction which enables them to grow and multiply. Carbon sources provide electrons during this process and are considered electron donors. For aerobic bacteria, the oxygen is the terminal acceptor of the electrons; but if oxygen is not present or is available in limited quantities, or if the bacteria respire anaerobically, some other receiver must be available for the electrons. There are a number of possible receivers of the electrons such as nitrate, sulfate, and iron (III) and manganese (IV). This experiment focuses on one possible receiver of those electrons, the iron (III) ion.

Iron reduction occurs in a variety of natural and anthropogenic settings, such as deep aquifers, lake and ocean sediments, swamps, oil spills, landfills—anywhere organic matter (food for the bacteria) and iron (III) coexist without oxygen. The iron oxides that contain the iron (III) ions are found in high concentrations in landfills because of the abundance of solid waste that contains solid elemental iron. When these materials interact with the water and air in the environment, the iron rusts forming iron oxides. In the landfill environment, where there is an abundance of organic matter and little available oxygen within the fill, anaerobic bacteria may respire the iron minerals. In other words, these bacteria use the iron (III) as the electron receivers during the respiration process. Oil spills and eutrophication are additional anaerobic situations that may provide conditions favorable for iron (III) respiration by bacteria.

Iron (III) does not dissolve in water and is mainly found in iron (III) minerals. These minerals, such as goethite (FeOOH) and hematite (Fe_2O_3) are responsible for the yellow and red colors of soils all across the planet and even on Mars.

3. Microbe-Mineral Interactions

National Standards

Nano2Earth Lessons	NSES Standards Addressed
Mineral-Microbe Interactions	
Engage: Prelab Questions	Unifying Concepts
Explore: Winogradsky Column Lab	<ul style="list-style-type: none">• Systems• Evidence• Models• Explanations• Changes• Measurement
Explain: Discussion and Sharing of Results	Science as Inquiry
Elaborate: Groundwater Scenario	<ul style="list-style-type: none">• Identify Questions and Concepts that Guide Scientific Explanations• Design and Construct Scientific Investigations• Using Technology and Mathematics to Improve Investigations and Communications• Formulate and Revise Scientific Explanations and Models Using Logic and Evidence
Evaluate: Analysis and Conclusions	Physical Science
	<ul style="list-style-type: none">• Structures and Properties of Matter• Chemical Reactions
	Life Science
	<ul style="list-style-type: none">• The Interdependence of Organisms• Matter, Energy, and Organization of Living Systems
	Earth and Space Science
	<ul style="list-style-type: none">• Geochemical Cycles
	Science in Personal and Social Perspectives
	<ul style="list-style-type: none">• Environmental Quality• Natural and Human Induced Hazards• Science and Technology in Local, National, and Global Challenges

Engage: Prelab Questions (Estimated time: 25 minutes)

These questions are designed to get the students to think about what they may already know about bacteria, respiration, and water quality. Students can be arranged into small groups to discuss the questions followed by a whole class discussion led by the students.

1. Where do you think the dissolved oxygen that is present in rivers, streams, ponds, and lakes originates?

The dissolved oxygen present in water on the earth's surface comes from oxygen in the air that is dissolved in the surface water and from the production of oxygen by water plants during their photosynthesis process.

2. Which type of bacteria, aerobic or anaerobic, do you think would be best adapted for survival in the water column of a stream? Which type is best adapted to survive deep in the muddy region of the stream? Make sure you can explain your choice.

Since dissolved oxygen is present in the water, aerobic bacteria would be successful surviving in this oxic region of the water. Since little dissolved oxygen is present within the muddy anoxic layer, anaerobic bacteria would be best adapted for this environment.

3. Make a prediction: What do you think will happen to the level of dissolved oxygen in a river if the river has an abundance of algal growth that is in the process of dying and decaying? Make sure you can explain your answer. Do you know what this process is called?

Students will have their own predictions for this question depending on their prior knowledge. During the decay of overabundant algal growth, oxygen is used which decreases the dissolved oxygen available for the other aquatic life dependent upon dissolved oxygen for survival. This decay process is called eutrophication. Eutrophication is a natural process, but if the level of eutrophication is excessive, the water becomes unhealthy for other organisms living in the water.

4. Make a prediction: Which type of bacteria, aerobic or anaerobic, would be best suited in the water environment that has an abundance of algal growth that is in the process of dying and decaying? Make sure you can explain your answer.

Anaerobic bacteria would be best suited for a water environment which is excessively eutrophic because of the lack of oxygen.

Explore: Winogradsky Column Lab (Estimated time: Varies from day to day)

During this activity, students will build a surface water ecosystem. The ecosystem will be used to:

1. Observe general visual changes that take place in the Winogradsky column over time
2. Simulate eutrophication
3. Observe the effect of excess nutrients on the dissolved oxygen concentration
4. Measure and follow changes in dissolved oxygen concentrations over a period of time
5. Relate changes in dissolved oxygen to water quality and microbial activity
6. Observe changes in Fe^{3+} to Fe^{2+} when the column becomes anaerobic
7. Relate mineral-microbial activity to water quality

This lab involves the creation of the Winogradsky columns, which are simply 20-24 oz. plastic bottles containing natural water and sediment. The water/mud samples may be collected before class by the teacher or during class by the students. Once the bottles are loaded, photosynthetic organisms should grow. They will begin to die and decompose as nutrients are exhausted. Sugar is added to encourage this process to proceed quickly, such that students will be able to measure and observe drastic changes in only a few days. The oxygen will be consumed, creating an anaerobic environment. Students will measure the amount of dissolved oxygen using probeware over a period of several days to monitor this transition. They will also add iron(III) chloride to create iron minerals in the water, which can be seen as a yellow-orange-red color. Students can observe how color changes in the water relate to the disappearance of oxygen. Finally, some students may add fertilizer to simulate the process of eutrophication.

3. Microbe-Mineral Interactions

Materials and Lesson Preparation

The procedure is outlined in the student handout; however, the following considerations should help make for a successful learning endeavor.

- Students will need to bring their own 20-24 oz plastic bottle. It should be rinsed out thoroughly and must have the cap.
- It would be most efficient if each group could have their own widemouth funnel.
- Any small container can be used in place of the 50-ml beaker.
- If the students are not able to get the mud and water themselves at a creek, the teacher will need to collect the mud and water ahead of time. It is best if it is collected the morning that it will be used. Enough mud should be collected so that the students can put about 2-3 inches in their bottles. Enough water should be collected so that all of the bottles can be filled after adding the mud-water mix. The mud-water can be taken from any local pond, lake, river, or stream. If the class is building the columns inside the classroom, make sure to put down a lot of newspapers in the work space.
- Only one dissolved oxygen probe is necessary; however, if more than one is available, it will speed up the measuring of the dissolved oxygen concentration in the bottle contents. Using dissolved oxygen kits that depend on a color comparison will not work because of the color of the mix interferes with testing. If dissolved oxygen probes are not available, students may complete the lab by observing color changes as an indication of mineral-microbial activity.
- The nutrients added to some of the columns can be any household fertilizer. Miracle-Gro® is an example of the type of fertilizer that can be used.

Teacher notes for each day of experiment

Day 1 (The amount of time needed for Day 1 will depend on how much preparation is done by the teacher ahead of time, as well as how many dissolved oxygen probes are available for the students.)

- Needless to say, this is a messy project! Newspapers should be put down at each work station. If possible, the bottles should be filled outside. Running water and a sink are necessary for cleaning up the outside of the bottles and the students. If the teacher collected the mud and water before school, the bottles of water should be sealed tightly, and the mud and water should be placed in an environment at the same temperature as the body of water from which they were taken earlier in the day.
- Each teacher will need to have their own directions about the use of the dissolved oxygen probe. With one probe available, each team can take their bottle to a station set up with the computer and probe to make the measurement. Oxygen will reenter the water in the bottle once it is opened, therefore, it is important to measure the DO concentration as soon as possible after opening the bottle. Students may want to open their bottles but then recap them until it is their turn to use the DO probe. Real-time reading of the DO level is fine. Let the probe stay in the muddy water until the DO concentration reading stabilizes. The teacher will probably have to talk a little bit about the DO concentration units. Have the students rinse off the probe with water after they are finished.
- Ask about half of the groups to add the Miracle-Gro® to their bottles.

Example of what students may write when observing bottles on day 1:

Sample observations:	Bottle without Miracle-Gro®	Bottle with Miracle-Gro®
DO concentration	7.5 mg/L	8.0 mg/L
Other observations	Mud settles to bottom of bottle. Water is cloudy above the muddy layer. The water layer in the bottle with fertilizer has a greenish color.	

Day 2 (Should immediately follow Day 1. This will take 15-30 minutes depending on how many probes are available for student use.)

- Visual changes in the bottles: Further settling has occurred with the mud. The water level will be clearer. The color of the water layer probably has not changed much. Students may notice that the bottle feels harder due to the gas pressure building up in the bottle.
- Some gases from the decomposition process may have built up at this point, so it is vital that the removal of the cap be a careful, slow, and supervised process. Doing this outside may be preferable. Putting the bottle down inside a sink may also help.
- Make sure the students wear safety goggles when using the iron (III) chloride.

Example of what students may write when observing bottles on day 2:

Sample observations:	Bottle without Miracle-Gro®	Bottle with Miracle-Gro®
DO concentration	6.9 mg/L	7.4 mg/L
Other observations	The iron (III) chloride turns the small sample of water a deep yellow color. When added to the bottle, it will give the water a more yellow color. The bottle w/ Miracle-Gro® may have a more greenish-yellow color due to the fertilizer. Small bubbles may rise from the muddy layer when the bottles are opened. The distinct odor resulting from the decomposition process may also be present.	

Day 3 (Should immediately follow Day 2. The amount of time needed for this part will depend on the number of DO probes available for student use.)

- Visual changes in the bottles: The bottle without the fertilizer will now have a reddish-orange color. The bottle with the fertilizer will not show any color change. The red-orange color is due to the iron (III) ions forming very small particles of iron hydroxides. Both bottles may feel harder because of the build up of gases in the bottle.

Example of what students may write when observing bottles on day 3:

Sample observations:	Bottle without Miracle-Gro®	Bottle with Miracle-Gro®
DO concentrations	1.9 mg/L	1.4 mg/L
Other observations	The bottle without the fertilizer is now a reddish-orange color. The bottle with the fertilizer did not change color. Both bottles have a gas build up inside the bottle. Bubbles rise from the mud when the bottle is opened. Distinct odors are evident from each bottle.	

3. Microbe-Mineral Interactions

Day 4 (Ideally, Day 4 would be the day that the red-orange color has faded. This may not immediately follow Day 3. The amount of time needed for this day will depend on the number of probes available for student use.)

- Visual changes in the bottles: The red color in the bottle without the fertilizer has faded. The red-orange color fading is due to the iron hydroxides converting into iron (II) ions which are soluble and colorless in water. The iron (II) is produced because the iron (III) has received electrons as a result of the bacteria's respiration process. The bottle environment has become anaerobic, so oxygen cannot function as the final receptor of the electrons during respiration. The bottles feel harder because of gas pressure building up in the bottle.



Example of what students may write when observing bottles on day 4:

Sample observations:	Bottle without Miracle-Gro®	Bottle with Miracle-Gro®
DO concentrations	0.8 mg/L	1.2 mg/L
Other observations	The bottle without the fertilizer has lost its red color. There is little to no change in the color of the bottle with the fertilizer. The bottles are hard due to the build up of gases. More bubbles rise from the mud when the bottle is opened. Odors are becoming stronger.	

- Cleaning up the bottles and contents: The bottle contents can be safely disposed of outside or in the waste going to the landfill. Cap the bottles and place in the trash.

Explain: Discussion and Sharing of Results (Estimated time: 20 minutes)

Have all students present their results to the class, including the DO concentrations and color changes over each day. The teacher should make a compilation of the results that can be seen by all of the class. These results will be necessary for answering the analysis and conclusions section below.

Elaborate: Groundwater Scenario (Estimated time: 30 minutes)

This scenario extends the concepts from the Winogradsky column to a realistic environmental problem. If toxic substances, such as arsenic, are present in the environment, respiration of iron (III) minerals in soils and sediments becomes a problem. Many contaminants such as arsenic bind strongly to the surface of the iron oxides (they are adsorbed). However, if the iron (III) is reduced by bacteria, it becomes iron (II) and, thus, soluble in water. When the iron compounds dissolve, they release the arsenic from their surfaces (it desorbs), so it will move into the groundwater.

Evaluate: Analysis and Conclusions (Estimated time: 20 minutes)

1. Why was the sugar added to the bottle?

The bacteria convert the sugar (organic matter, carbohydrates) and oxygen to carbon dioxide and water during the respiration process. The addition of the sugar also helps to ensure that the oxygen is used up quickly, so that the lab will only take a short time. This may represent an accelerated version of what might happen in a natural system.

2. What happened to the concentration of dissolved oxygen during the time period that you observed the DO level?

Students will have own answers for this question. The DO concentration in the bottle should have dropped.

3. Check with other lab groups to find out how the level of DO changed in their bottles during the experiment. Write down each group's result. Make sure to include whether or not they added Miracle-Gro® to their bottle. Do their changes agree with yours?

All of the groups should have observed a drop in the DO.

4. What caused this change in the dissolved oxygen concentration during the experiment?

The drop in DO level is caused by the oxygen being used by the aerobic bacteria during their respiration process and by other organisms during decomposition of organic matter in the bottle (such as dead bacteria and plant matter). Since the bottle is closed, there is no chance for the renewal of the oxygen in the water that would occur naturally when a creek is in contact with the air. Also, there are no water plants in the bottle actively replenishing the water with oxygen during the photosynthesis process.

5. Is there a difference in the dissolved oxygen change for the bottles that had Miracle-Gro® added and those without Miracle-Gro®? What do you think caused this difference?

The DO level in the environment containing the fertilizer may drop sooner and lower because of the excess nutrients in the water encouraging a more rapid rate of bacterial respiration. The lack of these nutrients might have been limiting bacterial growth.

6. Miracle-Gro® is considered a nutrient because it “feeds” the process of algal growth (an algal bloom) in bodies of water. Can you think of other nutrients that humans unintentionally add to rivers and lakes that stimulate the growth of algal blooms?

Nutrients that humans may add to water systems include excess fertilizer runoff from farms, yards, golf courses, agricultural runoff (animal manure), contents from leaky septic systems, and discharges from sewage systems.

3. Microbe-Mineral Interactions

7. When the algae dies and decomposes it causes eutrophication in the water. What happens to the level of dissolved oxygen in the body of water when eutrophication occurs? What problems do you think would be associated with excessive eutrophication?

During eutrophication, the level of dissolved oxygen decreases, thus, a reduced amount of oxygen is available for the aquatic life. This reduced amount of oxygen creates an unhealthy, or possibly toxic, environment for the aquatic life.

8. What part do you think you and your families can play in keeping excessive nutrients from finding their way into surface waters such as lakes, rivers, streams and ponds?

Students can encourage the correct and limited use of fertilizers in their yards or fields, encourage their parents to maintain an effective septic system, and keep their cattle and other livestock away from creeks and creek banks.

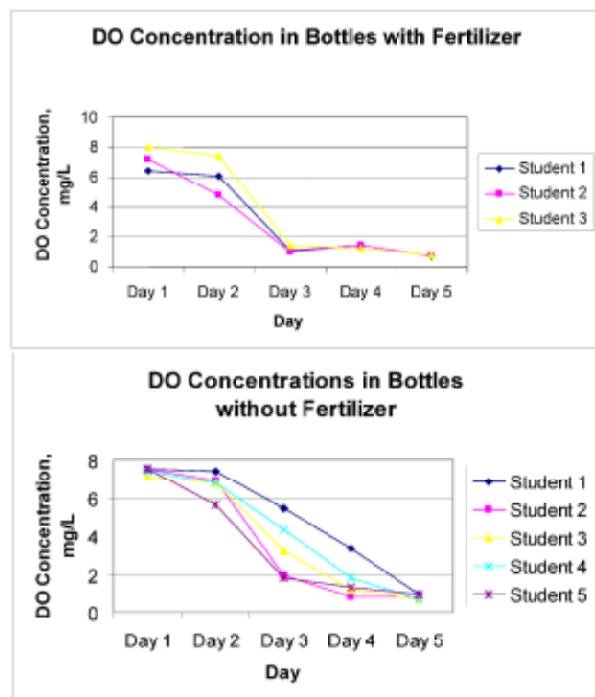
9. Adding the Fe^{3+} caused the solution to initially become a deeper or darker yellow color. What happened to this color during the experiment? What could have caused this change in color?

The dark yellow color changed to a red-orange, then disappeared. The yellow color was caused by the presence of Fe^{3+} in the water. The reddish-orange color was a result of the presence of small particles of iron hydroxide in the water. The disappearance of the color indicates that the Fe^{3+} is gone. It actually has converted into Fe^{2+} , which is soluble and colorless in water. This conversion of Fe^{3+} to Fe^{2+} during the reduction process (electrons being gained by the Fe^{3+}) causes the color to change from yellow/red to colorless.

10. During aerobic respiration, the oxygen is the terminal electron acceptor. When the bottle contents lacked oxygen, what do you think the terminal electron acceptor was during the respiration process?

During the experiment the color of the water above the mud went from brownish to yellow to red/orange then back to brownish after the iron (III) chloride was added. The yellow color was due to the presence of the iron (III) ion in the water which was converted into iron (III) oxide (red-orange). The fading of the red-orange color was due to the reduction of the iron (III) to iron (II). The iron (III) was the terminal electron acceptor.

Sample set of class results



Microbe-Mineral Interactions

Nano2Earth Activity Sheet

Using the Winogradsky Column to Demonstrate the Microbial Reduction of Iron (III) Activity

Prelab Questions

Get into groups of four students and discuss the following questions. Prepare to discuss your answers with the rest of the class.

1. Where do you think the dissolved oxygen that is present in rivers, streams, ponds, and lakes originates?
2. Which type of bacteria, aerobic or anaerobic, do you think would be best adapted for survival in the water column of a stream? Which type is best adapted to survive deep in the muddy region of the stream? Make sure you can explain your choice.
3. Make a prediction: What do you think will happen to the level of dissolved oxygen in a river if the river has an abundance of algal growth that is in the process of dying and decaying? Make sure you can explain your answer. Do you know what this process is called?
4. Make a prediction: Which type of bacteria, aerobic or anaerobic, would best be suited in the water environment that has an abundance of algal growth that is in the process of dying and decaying? Make sure you can explain your answer.

Experiment

Material and equipment needed for each group:

clean, 20-24 oz plastic bottle (with cap)	large opening funnel
mud and water from a pond, creek, or lake	1/2 tsp table sugar
1/8 tsp, pea sized portion, iron (III) chloride, FeCl ₃	50-ml beaker
1/4 tsp Miracle-Gro® (needed for half of the groups)	scoops or spoons for muddy water

Material and equipment needed for the entire class:

Vernier LabPro, dissolved oxygen probe	buckets for mud and water
window or grow-lamp	1/4 tsp measuring spoon

Safety considerations

- Students need to wash their hands after building the column and anytime they have worked with the column.
- Safety goggles are needed on Day 2 and Day 3 because students will be working with iron (III) chloride, and Miracle-Gro®

Microbe-Mineral Interactions Nano2Earth Activity Sheet

Procedure

Day 1

1. If your **teacher has already prepared** your mud/water mixture for you, you are ready to put it in the plastic bottle. Place the large opening funnel in the open end of the plastic bottle and use a spoon to add the mud/water mixture to the bottle. Add the mixture until it reaches about 3 inches.

If your **teacher has not gotten the mud/water mix ready** for you,

then you need to prepare it yourself. Using a heavy spoon, dig mud from the pond bottom and put it

in a bucket or bowl. Add water to make the mud/water mix thick but able to be spooned into the funnel. Place the funnel into the opening of the bottle and spoon the mud/water mix into the bottle to a height of about 3 inches.

2. Add pond water to the bottle until the bottle is nearly full.
3. Using the dissolved oxygen probe, follow your teacher's directions for measuring the dissolved oxygen concentration of the bottle environment. Record the results in the data table.
4. Add $\frac{1}{2}$ tsp of table sugar (sucrose) to the bottle. **Gently tilt** the bottle to mix the sugar with the water in the bottle.
5. The teacher will let you know if your group is going to also add Miracle-Gro® to the bottle. If your bottle is to contain Miracle-Gro®, add about $\frac{1}{4}$ tsp to the bottle. Gently tilt the bottle to mix the fertilizer with the contents of the bottle.



Microbe-Mineral Interactions

Nano2Earth Activity Sheet

6. Cap the bottle and place the bottle near a window. Do not put the bottle in direct sunlight. If a window is not available, place the bottle about 2 feet from a 40-60 Watt light bulb, or near a grow lamp.
7. Take a few minutes to observe the bottle. Record your description of the contents in the data table.

Day 2

1. Examine your bottle. What do you observe? What is different from Day 1? Record your observations on the Day 2 data table.
2. Place your bottle down inside a sink. Very carefully and slowly, loosen the cap of the bottle. Make sure to keep under control any bottle contents that attempt to squirt out of the bottle. Remove the cap from the bottle.
3. Follow your teacher's directions to find the dissolved oxygen concentration of the bottle contents. Record the result in the data table.
4. Mix pea size, or 1/8 tsp, of iron (III) chloride to a small amount of water in a 50-ml beaker or small cup. Note the color of this Fe^{3+} solution and record in the data table. Add this solution to the bottle. You may need to gently pour out a little bit of the water in the bottle to make room for the iron (III) solution. Let the bottle sit for a few minutes undisturbed. Note the color of the water in the bottle and record in your data table.

Day 3

1. Examine your bottle for changes since Day 2. Record your observations in the data table.
2. Place the bottle in a sink and very carefully and slowly twist the cap off.
3. Measure the concentration of dissolved oxygen in the bottle contents. Record the value in the data table.

Day 4

1. Examine your bottle for changes since Day 3. Record your observations in the data table.
2. Place the bottle in a sink and very carefully and slowly twist the cap off.
3. Measure the concentration of dissolved oxygen in the bottle contents. Record the value in the data table.
4. Follow your teacher's directions for cleaning up the bottles

Microbe-Mineral Interactions
Nano2Earth Activity Sheet

Data Tables

Our bottle **did/did not** (circle one) have Miracle-Gro® added to it.

Day 1

Dissolved oxygen concentration	Description of bottle contents

Day 2

Description of bottle contents	Dissolved oxygen concentration	Color of iron (III) solution	Color of bottle after iron (III) added

Microbe-Mineral Interactions
Nano2Earth Activity Sheet

Day 3

Dissolved oxygen concentration	Description of bottle contents

Day 4

Dissolved oxygen concentration	Description of bottle contents

Microbe-Mineral Interactions Nano2Earth Activity Sheet

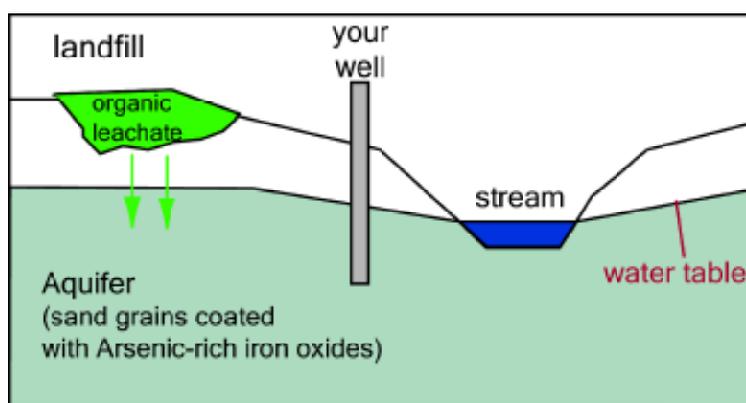
Groundwater Scenario

Your town's aquifer (naturally stored water underground) consists of sediments that were deposited in an ancient river system like the Mississippi delta. The sediments consist of quartz grains coated with iron oxides. Analysis of the sediments shows that it contains trace concentrations of arsenic, but when you analyze the groundwater, it does not contain arsenic. How would you explain this difference in the presence of arsenic?

The municipal landfill for your town has been collecting garbage for 50 years. In addition to paper, plastic, and metal, there is also a lot of food and compost waste. In other words, the landfill is rich in organic matter. Rainwater percolates through the landfill and the leachate (mixture of rainwater and other dissolved materials from the landfill) easily gets into the groundwater.

Your family's well is located near the landfill. Recently you noticed that the water tastes like iron. You have the well water analyzed and find that it contains arsenic. Where do you think the arsenic is originating?

The diagram may help you to imagine the scenario:

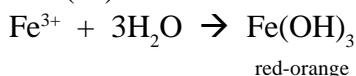


Equations that may help:

aerobic respiration:



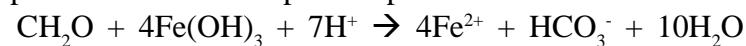
iron (III) reacts with water



iron (III) chloride dissolved in water:



possible anaerobic respiration process:



red-orange

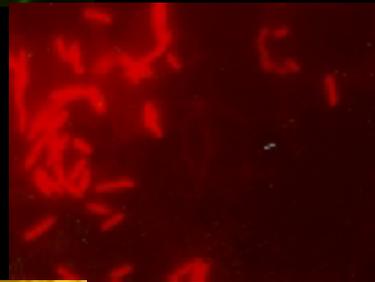
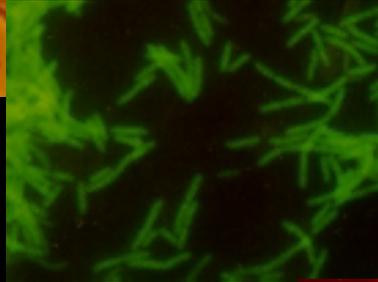
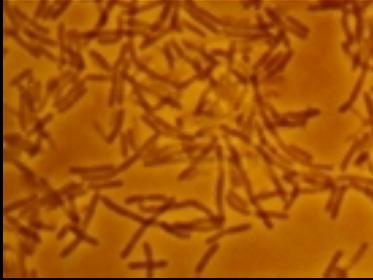
colorless

Microbe-Mineral Interactions

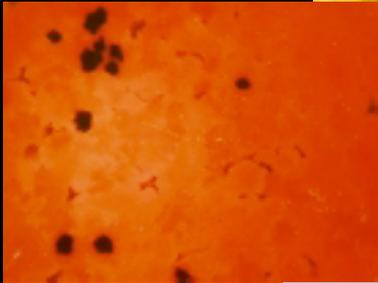
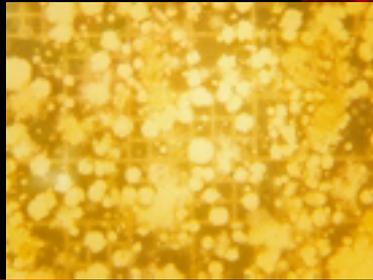
Nano2Earth Activity Sheet

Analysis and Conclusions

1. Why was the sugar added to the bottle?
2. What happened to the concentration of dissolved oxygen during the time period that you observed the DO level?
3. Check with other lab groups to find out how the level of DO changed in their bottles during the experiment. Write down each group's result. Make sure to include whether or not they added Miracle-Gro® to their bottle. Do their changes agree with yours?
4. What caused this change in the dissolved oxygen concentration during the experiment?
5. Is there a difference in the dissolved oxygen change for the bottles that had Miracle-Gro® added and those without Miracle-Gro®? What do you think caused this difference?
6. Miracle-Gro® is considered a **nutrient** because it “feeds” the process of algal growth (an algal bloom) in bodies of water. Can you think of other nutrients that humans unintentionally add to rivers and lakes that stimulate the growth of algal blooms?
7. When the algae dies and decomposes it causes eutrophication in the water. What happens to the level of dissolved oxygen in the body of water when eutrophication occurs? What problems do you think would be associated with excessive eutrophication?
8. What part do you think you and your families can play in keeping excessive nutrients from finding their way into surface waters such as lakes, rivers, streams and ponds?
9. Adding the Fe^{3+} caused the solution to initially become a deeper or darker yellow color. What happened to this color during the experiment? What could have caused this change in color?
10. During aerobic respiration, the oxygen is the terminal electron acceptor. When the bottle contents lacked oxygen, what do you think the terminal electron acceptor was during the respiration process?



Various microscopic techniques used to image iron-reducing bacteria are shown here



Lesson 4

Investigation of Bacterial Transport in Groundwater

Purpose

The students will explore the transport of bacteria in groundwater by performing a column experiment in a simulated groundwater environment. Students will also investigate a groundwater scenario to learn about the influence of groundwater chemistry on bacterial transport.

Background Information

Bacteria transport is an important area of research in the study of groundwater pollution. As bacteria play an important role in causing disease, understanding particle transport and its environmental effects is important for addressing water quality, bioremediation, and global health issues. Bacteria are transported through porous materials as a function of physical and chemical properties of the microbes, minerals, and water. In this laboratory experiment, small microbeads, representing bacteria, are passed through a column of coarse sandy material. Effluent is collected and analyzed using absorption and/or reflectivity by means of the light sensor probe. The results are graphed and interpreted to find the number of microbeads that become trapped in the column and the number that are passed through the system.

Following the lab, students will investigate a groundwater pollution scenario in which the concepts of surface charge and single displacement reactions are addressed in relation to the groundwater chemistry of particle transport. In lesson 5, students will see how the nanoscale forces (electrostatic and Van der Waals forces) between charged surfaces can be measured with an important tool of nanotechnology, the Atomic Force Microscope (AFM). In preparation for lesson 5, teachers may review the concepts of nanoscale science and technology (see chapters 1-3).

National Standards

Nano2Earth Lessons	NSES Standards Addressed
<p>Investigation of Bacterial Transport in Groundwater</p> <p>Engage: Groundwater Pollution Scenario and Waterborne Diseases</p> <p>Explore: Bacterial Transport in a Sand Column</p> <p>Explain: Class Discussion and Questions</p> <p>Elaborate: Influence of Groundwater Chemistry on Bacterial Transport</p> <p>Evaluate: Groundwater Pollution Scenario Revisited</p>	<p>Unifying Concepts</p> <ul style="list-style-type: none"> • Systems • Evidence • Models • Explanations • Changes • Measurement <p>Science as Inquiry</p> <ul style="list-style-type: none"> • Identify Questions and Concepts that Guide Scientific Explanations • Design and Conduct Scientific Investigations • Using Technology and Mathematics to Improve Investigations and Communications • Formulate and Revise Scientific Explanations and Models Using Logic and Evidence <p>Physical Science</p> <ul style="list-style-type: none"> • Structures and Properties of Matter • Motions and Forces

4. Investigation of Bacterial Transport

Earth and Space Science

- Geochemical Cycles

Science in Personal and Social Perspectives

- Environmental Quality
- Natural and Human Induced Hazards
- Science and Technology in Local, National, and Global Challenges

Materials

- Light sensor probe (CBL or computer based laboratory, PASCO, LabPro)
- 2 micrometer fluorescent carboxylated microbeads can be ordered from Polysciences, Inc. They are called Fluoresbrite™ Yellow Green (YG) carboxylate microspheres, catalog number 09847 for a 5 mL bottle (~\$120). Alternatively, a 1 mL trial size may be ordered (~\$43). For the experiment, 0.1 mL will be needed for each group.
- Bag of coarse sand (playground) purchased at a hardware or home supply store. Rinse thoroughly before giving to students to remove fine materials. Fine suspended material can flush through the column during the experiment and interfere with the light sensor measurements.
- For the Elaboration activity, pH paper and 10 mL 0.1M HCL will be needed for each group.
- Each group should bring to class:
 - 16 oz or 20 oz plastic soda bottle (bottom will be cut off in lab)
 - small flashlight or pen light

Science Safety

This activity requires group work, and the teacher will facilitate student progress and experimentation. The Elaborate activity will use weak hydrochloric acid. Students are required to wear safety goggles. The teacher should carefully supervise cutting off the bottle bottoms and poking holes in caps. It is recommended that the teacher practice this beforehand prior to demonstrating to students.

Engage: Groundwater Pollution Scenario (Estimated time: 15 minutes) and Waterborne Diseases (Estimated time: 20 minutes)

Procedure

1. The teacher will engage the students in learning about particle transport by discussing a groundwater pollution scenario and sources of waterborne diseases. This activity should be done as a pre-lab. The purpose of the Engage activity questions is to get the students to think about what they may already know about bacteria and water quality. Students can be arranged into small groups to discuss the questions followed by a whole class discussion.

2. Student should read and discuss the handout: Waterborne Diseases (20 minutes)

Answers to Engage Activity Questions

1. What are the potential sources of the *E. coli* in your well?

Potential sources of the E. coli are your septic system, your neighbor's septic system, and farm animals.

2. Groundwater flows 1 m a day. Your neighbors live ~ 100 m down the hill from you. Look at the figure to see the direction of groundwater flow. How long would it take for bacteria from your well to reach your neighbors' houses?

$v=d/t$, $v = 1 \text{ m/d}$, $d=100 \text{ m}$; $t = v/d = 1 \text{ m/d} / 100 \text{ m} = 100 \text{ days}$ /it would take 100 days to get to your neighbor's house.

3. What factors do you think might control how the bacteria are being transported in groundwater?

Factors that control bacterial transport include: type of rock, porosity and permeability, structures or folds/faults in rock, preferential flow, type of bacteria, number of bacteria, chemical characteristics of groundwater, direction of water flow, velocity of water flow.

Explore: Bacterial Transport in a Sand Column (Estimated time: 1.5 hours)

1. Setup procedure: teacher should set up everything ahead of time but the actual column (students will do this). (45 minutes)
2. Students should use the light probe to collect data. (30 minutes)
3. Using the data collected with the probe, students should construct graphs to determine the concentration of particles (microbeads). (15 minutes)

Explain: Class Discussion and Questions (Estimated time: 30 minutes)

Students should answer and discuss the questions related to bacteria transport lab.

Explain Activity Questions

1. Based on your data, would adding more microbeads to the solution increase or decrease the light intensity value?

Decrease

2. Why does light intensity decrease when the microbead concentration increases?

Less light shines through because the fluid is filled with microbeads

4. Investigation of Bacterial Transport

3. Calculate the number of microbeads that remain in the column of sand.

The number depends on results of experiments.

4. Why did some of the microbeads remain in the column?

They get strained (filtered) or adhere/stick to the sand.

5. If a bacterium is 1-2 micrometers ($1 \text{ mm} = 10^{-6} \text{ m}$) in diameter, how does that mathematically compare to a nanoparticle? ($1 \text{ nm} = 10^{-9} \text{ m}$)

A bacterium would be 1000 nm.

6. Smoke particles, viruses, and some bacteria are nanoparticles. If we used nanobeads instead of microbeads in our experiment, would you expect them to behave differently than the microbeads? Why?

Smaller (nano) particles would likely pass through the system to a greater extent than larger (micro) particles due to filtration. Nanoparticles and microparticles have different surface to volume ratios, and that may change the attraction/repulsion properties of the particles to the surface, but the effect of this on transport is not clear. This is an area of current scientific research.

Elaborate: Influence of Groundwater Chemistry (pH) on Bacterial Transport (Estimated time: 2.5 hours)

Setup procedure: Students will follow the same procedure as in the Exploration activity, except they also will need pH paper and 10 ml 0.1 M HCl for each group. The actual lab should take 35-40 minutes and data graphing should take about 15 minutes. Students should answer and discuss the questions related to the Investigation of Bacterial Transport Lab.

Elaborate Activity Questions

1. Does adding 10 ml of HCl to the microbead solution raise or lower the pH?

It lowers the pH.

2. What happens to the surface charges on the sand and microbeads when pH is lowered? What happens to the surface charges when the pH is raised?

As pH decreases (becomes more acidic), the number of H^+ ions in solution increases. The free H^+ ions prefer to be associated with the negative charges on bacteria and mineral surfaces. Effectively, when solution pH is lowered, the surfaces of minerals and bacteria become more positively charged. When the pH is increased, the opposite happens – the surfaces become more negatively charged.

3. If you add a teaspoon of salt to the microbead solution, would you expect the surfaces to become more or less “sticky”?

They would become more sticky as higher ionic strength increases attractive forces between the bacteria and sediment.

4. Calculate the number of microbeads that remained in the column of sand.

The number depends on the results of experiments.

5. Do you think live bacteria would behave differently than the microbeads? Why? *Hint: Are ALL bacteria the same size and shape?

Live bacteria would behave differently than microbeads – they are different shapes and sizes, and some bacteria produce proteins and other compounds that help them to stick to surfaces.

6. Do you think sand accurately represents the rocks around your house and school? Explain.

Answers may vary – depends on the geology of the area.

7. List two differences between the sand column and the real rocks around your region.

Answers may vary based on the geology of the area.

8. When storms occur and flooding is evident, there are often concerns about drinking water purity. Why?

Several reasons. Floods can “strip” off bacteria from sediment into water. They can also bring runoff, e.g., from agricultural fields, to surface water. Also, because flood water is derived from rain, the water is more dilute, and bacteria stick less to sediment under lower ionic strength.

9. What would happen to the ionic strength of groundwater during a flood?

The groundwater would likely become more dilute. The ionic strength should decrease.

4. Investigation of Bacterial Transport

Evaluate: Groundwater Pollution Scenario Revisited (Estimated time: 1.5 hours)

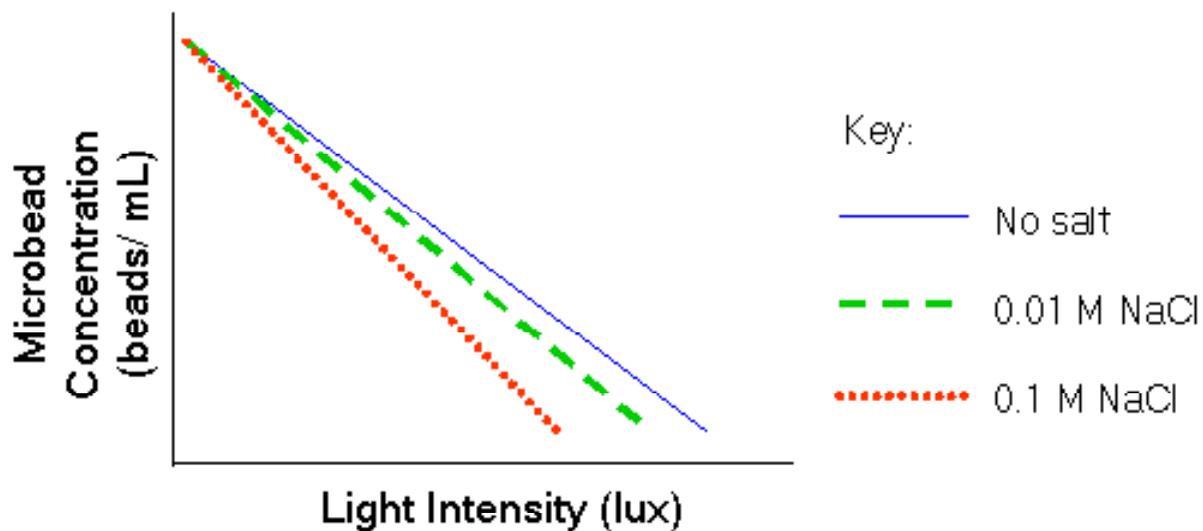
To gauge the students' understanding of how changing pH and ionic strength may affect bacterial transport, pose the following questions in relation to the original scenario (Engage activity). Encourage the students to draw diagrams supporting their answers, for example of the charge at the mineral and microbe surfaces in solution.

1. Consider that the ground beneath the pasture and housing development are made of:
 - a. Quartz sand (such as you would find on a beach)
 - b. Iron oxide-coated soil (such as any red or yellow soil you have seen)

How might bacterial transport be different in the two different soils?

To answer this question, it is necessary to know that at pH values of most soils and groundwaters, quartz has a negative charge on the surface and iron oxide minerals have a positive surface charge.

2. Ask the students to design an experiment to test the effects of ionic strength on bacterial transport using the microbeads. They may come up with ideas such as adding different amounts of NaCl or another salt to the microbead solution. Have the students predict what the results of these experiments will be and draw graphs representing the expected trends. Then have the students do the experiments, repeating the previous procedures with their modifications. How do the results compare with their predictions?

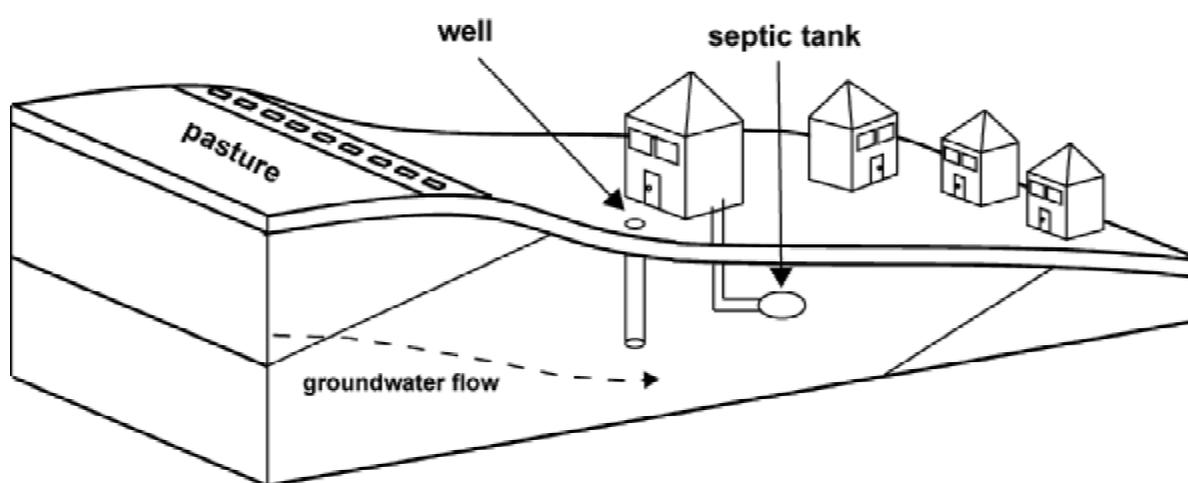


Example of student predictions

Investigation of Bacterial Transport Nano2Earth Activity Sheet

Engage: Groundwater Pollution Scenario

You have just moved into a subdivision in which all the houses have a well and a septic system (see figure below). Your house is located on the outskirts of the subdivision, right next to a cow pasture. You move in during the winter, when most of the cows are not out grazing, and things are fine. However, during the following spring, you get sick. The doctor tells you to analyze your well water for bacteria. You do, and it turns out that your well has *E. coli*, a pathogenic bacteria from fecal matter. You ask your three neighbors down the hill to have their wells tested. Results show that their wells are fine.



Questions:

1. What do you think are the potential sources of the *E. coli* in your well?
2. Groundwater flows 1 m a day. Your neighbors live about 100 m down the hill from you. Look at the figure to see the direction of groundwater flow. How long would it take for bacteria from your well to reach your neighbors' houses?
3. What factors do you think might control how the bacteria are being transported in groundwater?

Investigation of Bacterial Transport Nano2Earth Activity Sheet

Waterborne Diseases

Contamination of water supplies by pathogenic microorganisms is a leading cause of death in the world. It is estimated that 10 million people die every year from waterborne diseases, such as Typhoid, Cholera, and Dysentery. According to the World Health Organization, 19% of deaths from infection worldwide are water-related, and water-related diseases contribute to the death of nearly 4 million children each year. Kofi Annan, U.N. Secretary General, said on June 5, 2003: “One out of every 6 people lives without regular access to safe drinking water. Worse, water-related diseases kill a child every 8 seconds, and are responsible for 80% of all illnesses and deaths in the developing world”.

Waterborne Pathogens (from <http://www.mwra.state.ma.us>)

Diseases	Responsible pathogen	Route of exposure	Mode of transmission
Cholera	Vibrio cholerae bacteria	gastrointestinal	often waterborne
Botulism	Clostridium botulinum bacteria	gastrointestinal	food/waterborne; can grow in food
Typhoid	Salmonella typhi bacteria	gastrointestinal	water/foodborne
Hepatitis A	Hepatitis A virus	gastrointestinal	water/foodborne
Dysentery	Shigella dysenteriae bacteria or Entamoeba histolytica amoeba	gastrointestinal	food/water
Cryptosporidiosis	Cryptosporidium parvum protozoa	gastrointestinal	waterborne; resists chlorine
Polio	polioviruses	gastrointestinal	exposure to untreated sewage; may also be waterborne
Giardia	Giardia lamblia protozoa	gastrointestinal	waterborne

Part of the difficulty in controlling bacterial contamination of water supplies is that it is difficult to predict how bacteria are transported from one place to another. One thing we do know is that bacteria would rather be attached to a surface than floating in water. Surface attachment is a survival strategy. Not only does the surface provide a more stable environment, but it also allows the bacteria greater access to energy sources (e.g., carbon) and nutrients.

Investigation of Bacterial Transport

Nano2Earth Activity Sheet

Part 1. Bacterial Transport in a Sand Column

Purpose

The purpose of this lesson is to simulate how particles, such as bacteria, are transported through porous materials as a function of physical and chemical properties. Instead of using live bacteria, you will work with microbeads, which are a similar size and shape as bacteria.

Background Information

Particles, such as bacteria, have a diameter between 10 nm and 10 μm and are so small that they cannot be seen without a microscope. Due to their small size, bacteria have a very large surface area to mass ratio.

Bacteria can be removed from water by two mechanisms. They can be filtered (“strained”) out of solution through porous media (like sand in Figure 1 or limestone in Figure 2). This process is a function of the differences in size between the bacteria and the mineral grains in the rock. Bacteria can also be removed by adsorption onto surfaces. When water containing bacteria passes through the ground, some bacteria become stuck to the rocks and minerals in the ground and are removed from the solution. This can slow down bacterial transport in groundwater. It is a goal of scientists and engineers to be able to predict how far bacteria will travel in groundwater and how they attach to the rocks and minerals in the ground.

The “stickiness” of bacteria to rocks and minerals depends on several factors related to forces that act on particles that are as tiny as bacteria. These forces are a function of the chemistry of the groundwater and the types of particles and minerals that are present. Many bacteria and minerals have electrostatic charges on their surfaces which can sometimes be used to determine if the bacteria will stick to each other.

This experiment is a laboratory scale study of a real-life system. In this study, there is a release of bacteria onto a sandy soil and you need to determine how many bacteria have traveled through the soil. You will also relate your findings to several other real world situations. Environmental consultants get paid big bucks to do work just like this! Good luck and have fun!

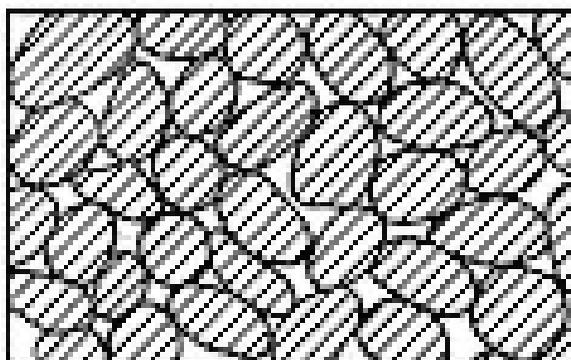


Figure 1. Pictured are pores between sand grains. If bacteria are bigger than the pore spaces, they can be filtered, or ‘strained’.

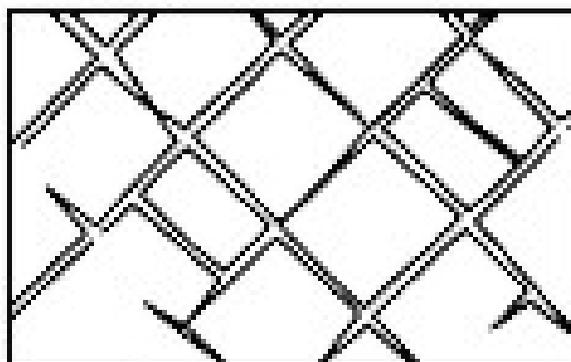
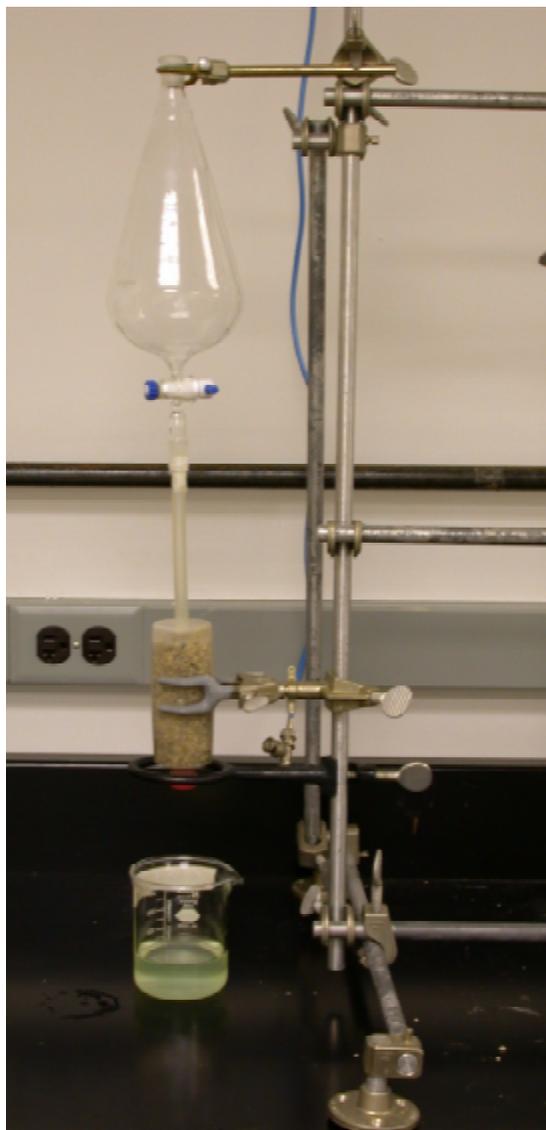


Figure 2. Fractures in rocks are depicted. Depending on the width of the fracture openings, bacteria can either be transported with water or they may be strained.

Investigation of Bacterial Transport Nano2Earth Activity Sheet

Materials and Resources (required for each lab setup)

Plastic column (16 or 20 oz bottle with bottom cut off)
Column fill (very coarse sand ~3-4 mm diameter)
Clean water
3 Glass beakers (250 ml)
Ring stand and clamp
Flashlight (a tightly focused penlight flashlight works best)
CBL light sensor probe
Tape
Microbeads (2 mm fluorescent carboxylated beads, 0.1 ml will be needed per lab group)
Graph paper



An example of a column experiment equipment setup is shown. It is not necessary to use the upper reservoir.

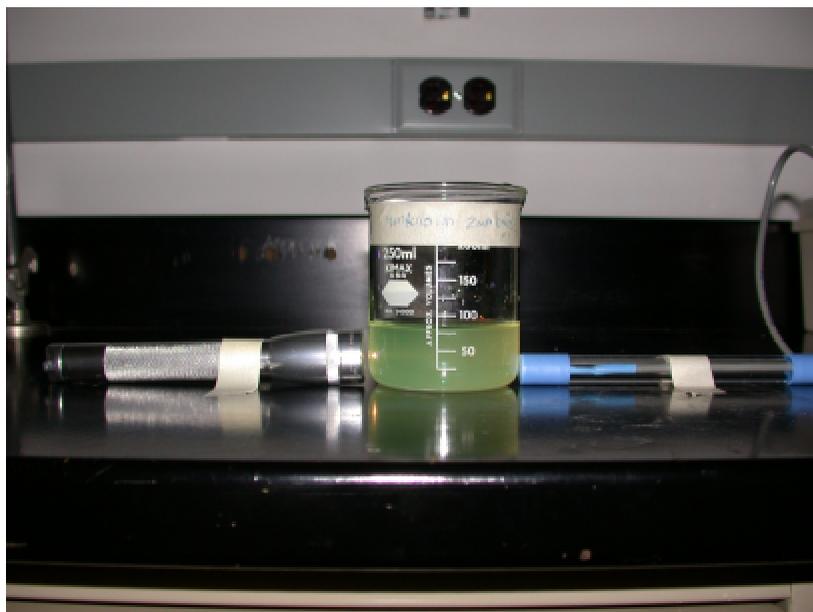
Procedure:

1. Fill the plastic column with very coarse sand and mount on the ring stand as shown in diagram.
2. Fill a 250 ml glass beaker with 100 ml of clean water.
3. Set up CBL light sensor probe, flashlight, and beaker with water as shown in diagram 2. Use the tape provided to secure the position of the probe and flashlight. Place a sheet of paper underneath the apparatus and outline the position of the glass beaker with a pen.
4. Align the beam from the flashlight into the light sensor probe.
5. Be sure the probe is connected to a data collector (i.e., computer or TI graphing calculator).
6. Measure the intensity of light as it passes from the flashlight through the beaker of water and into the light sensing probe. Collect light intensity (lux) for 10 continuous seconds. Record the average value. Leave the flashlight on and do not adjust the intensity coming from the flashlight.
7. Fill column with CLEAN water to saturate the sand. Collect any water that drains from the column in a large container and dispose in sink. Do not let the column drain completely. When the column starts to drip more slowly, put tape over the bottom to keep the column saturated.

Investigation of Bacterial Transport Nano2Earth Activity Sheet

8. Empty any remaining water from 250 ml beaker into sink and dry the beaker.
9. Label clean, dry beaker “unknown sample” and place under column. See diagram 1.
10. Retrieve 100 ml of microbead solution from teacher in a 250 ml glass beaker. Label the beaker “known sample”. NOTE: Your teacher has already diluted 0.5 ml of 4.5×10^{11} beads/ml solution into 500 ml. The known microbead concentration is 4.5×10^8 beads/ml.

11. Measure the intensity of light as it passes from the flashlight through the beaker containing the known sample and into the light sensing probe. Collect light intensity for 10 continuous seconds. Record the average value.



12. Pour known sample of fluorescent microbead solution into column slowly.

13. Effluent will be collected in beaker labeled “unknown sample”.

14. When approximately 100 ml of solution has collected in the beaker, remove the beaker from under the column and place in position to measure light intensity. Refer to diagram 2.

15. Collect light intensity for 10 continuous seconds. Record the average value.

16. Complete data table below:

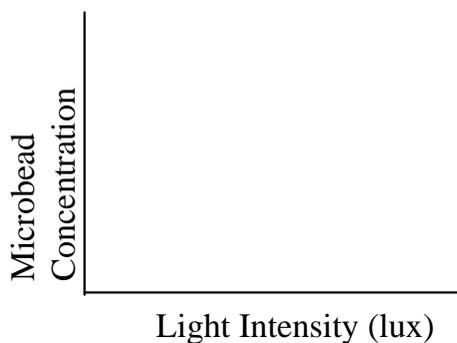
	Clean Water	Known Sample	Unknown Sample
Light Intensity (lux)			
Microbead Concentration	0	4.5×10^8 beads/ml	

17. Using data table above, plot microbead concentration (Y axis) versus light intensity (X axis) for the clean water and known sample on a sheet of graph paper. See diagram 3.

Investigation of Bacterial Transport

Nano2Earth Activity Sheet

Diagram 3. Example XY plot for calculating unknown sample concentration



18. Draw a straight line between the two points on your graph. Label this line the absorption line.
19. On the X axis, find the light intensity value of your unknown sample.
20. Draw a vertical line from the X axis to the absorption line.
21. From the point on the absorption line, draw a horizontal line to the Y axis and determine the microbead concentration.

Questions

1. Based on your data, would adding more microbeads to the solution increase or decrease the light intensity value?
2. Why does light intensity decrease when the microbead concentration increases?
3. Calculate the number of microbeads that remain in the column of sand.
4. Why did some of the microbeads remain in the column?
5. If a bacterium is 1-2 micrometers ($1 \text{ mm} = 10^{-6} \text{ m}$) in diameter, how does that mathematically compare to a nanoparticle? ($1 \text{ nm} = 1 \cdot 10^{-9} \text{ m}$)
6. Smoke particles, viruses, and some bacteria are nanoparticles. If we used nanobeads instead of microbeads in our experiment, would you expect more or less particles to remain in the column? Why?

Investigation of Bacterial Transport

Nano2Earth Activity Sheet

Part 2. Influence of Groundwater Chemistry (pH) on Bacterial Transport

Purpose

The purpose of this lesson is to examine the influence of groundwater chemistry on bacterial transport.

Background Information

It has already been stated that groundwater chemistry has a strong effect on how particles stick to surfaces. Why does this happen? It happens because most bacteria and mineral surfaces have electrostatic charges, and these charges are a function of pH and ionic strength. pH is a measure of the concentration of hydrogen ions in solution; it determines the acidity of a solution. Ionic strength is a measure of the concentration of charged atoms, or ions, in solution. Salty water has a large amount of Na^+ and Cl^- ions in solution and, therefore, has a high ionic strength. Groundwater pH and ionic strength can change due to the types of rocks present in the ground, precipitation, evaporation, and human use. Groundwater usually has a pH that is slightly acidic ($\text{pH} < 7$) and low ionic strength.

Mineral surfaces can be negatively or positively charged, depending on their atomic structure. Sand, which is made of the mineral quartz (SiO_2), is negatively charged in water at pH 7. The electrostatic charge of bacteria is also typically negative in water at pH 7 (Figure 1A). As pH decreases (becomes more acidic) the number of H^+ ions in solution increases (Figure 1B). The free H^+ ions prefer to be associated with the negative charges on bacteria and mineral surfaces. Effectively, when solution pH is lowered, the surfaces of minerals and bacteria become more positively charged. What do you think would happen to surface charge when pH is raised (becomes more basic)?

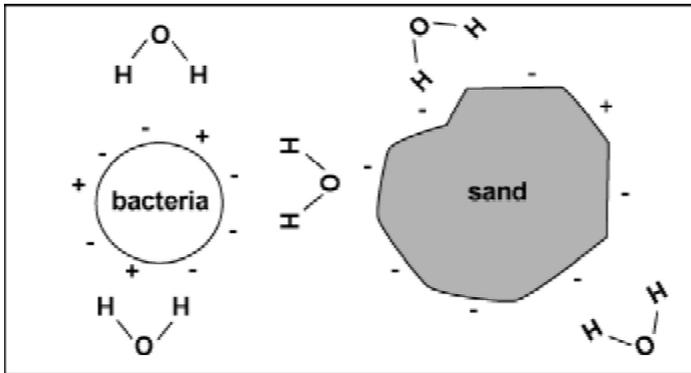


Figure 1A. At pH 7, most bacteria and sand grains are negatively charged.

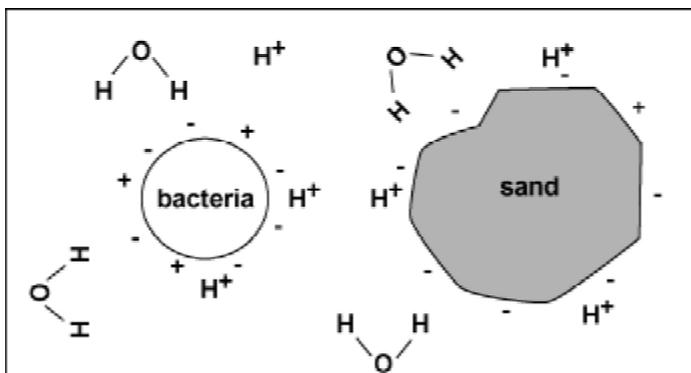


Figure 1B. At low pH, the number of H^+ ions in solution increases and surface charges change.

Investigation of Bacterial Transport

Nano2Earth Activity Sheet

Ionic strength also has an effect on surface charge. Pristine groundwater has low ionic strength. At low ionic strength, the surface charges on minerals and bacteria are loosely arranged around the surface (Figure 2A) in a region called the double layer. At high ionic strength, this double layer shrinks and mineral and bacterial surface charges are more tightly arranged around the surfaces (Figure 2B). When the double layer shrinks, repulsive forces become weaker and attractive forces become stronger. Bacteria and mineral surfaces become “stickier”.

Figure 2A. At low ionic strength, surface charges are loosely arranged around the mineral and bacterial surface. The double layer is shown in light grey.

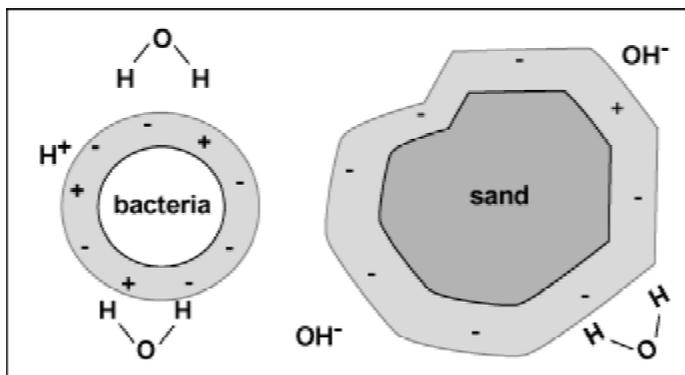
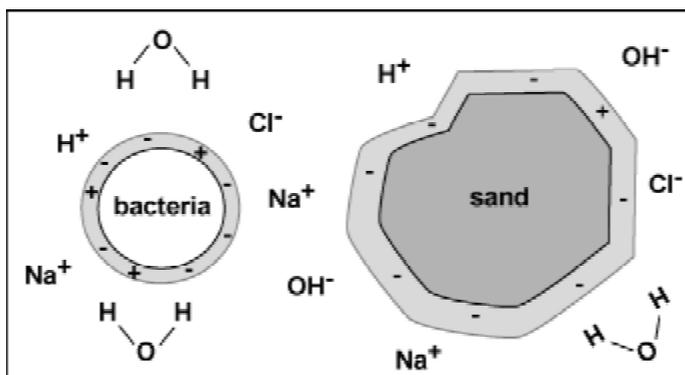


Figure 2B. At higher ionic strength, surface charges are more tightly associated with the mineral and bacterial surfaces.



Groundwater pH and ionic strength can vary significantly. Most groundwater is slightly acidic and has low ionic strength. Flooding, irrigation for farming, and drought can cause pH and ionic strength to change a lot. Human activities like construction, fertilizing, and salting roads in the winter can cause drastic changes in groundwater chemistry. Imagine the effects of large scale processes like mining!

This experiment is a continuation of the column experiment that investigated the number of microbeads that passed through a column of sand. Microbeads will be used again to model the behavior of real bacteria. The microbeads and sand grains used in the study have a net negative surface charge. In this experiment, you will change solution chemistry and measure the effect it has on microbead transport. You will relate your findings to more real life situations and predict how bacterial transport is affected by human activities. Let's get to work!

Investigation of Bacterial Transport

Nano2Earth Activity Sheet

Materials and Resources (required for each lab setup)

Plastic column (coke bottle with bottom cut off)
Column fill (very coarse sand ~3-4 mm diameter)
Clean water
3 Glass beakers (250 ml)
Ring stand and clamp
Flashlight (a tightly focused penlight flashlight works best)
CBL light sensor probe
Tape
Microbeads (2 mm fluorescent carboxylated beads, 0.1 ml will be needed per lab group)
Graph paper
10ml of 0.1M HCl
pH paper

Procedure

1. Fill the plastic column with very coarse sand and mount on the ring stand just as you did in part 1 (see diagram 1 of part 1).
2. Fill a 250 ml beaker with 100 ml of clean water.
3. Set up CBL light sensor probe, flashlight, and beaker with water as before (see diagram 2 of part 1). Remember to use tape to secure the position of the probe and flashlight. Place a sheet of paper underneath the apparatus and outline the position of the glass beaker with a pen.
4. Align the beam from the flashlight into the light sensor probe.
5. Be sure the probe is connected to a data collector (i.e., computer or TI graphing calculator).
6. Measure the intensity of light as it passes from the flashlight through the beaker of water and into the light sensing probe. Collect light intensity (lux) for 10 continuous seconds. Record the average value. Leave the flashlight on and do not adjust the intensity coming from the flashlight.
7. Fill column with the 100 ml of CLEAN water to saturate the sand. Collect any water that drains from the column in a large container and dispose in sink. Do not let the column drain completely. When the column starts to drip more slowly, put tape over the bottom to keep the column saturated.
8. Empty any remaining water from the beaker into the sink. Dry the beaker.
9. Label the clean, dry beaker “unknown sample part 2” and place under column.
10. Retrieve 90 ml of microbead solution from teacher in a 250 ml glass beaker. Label the beaker “known sample”.
11. Add 10 ml of weak HCl acid to the 90 ml microbead solution.

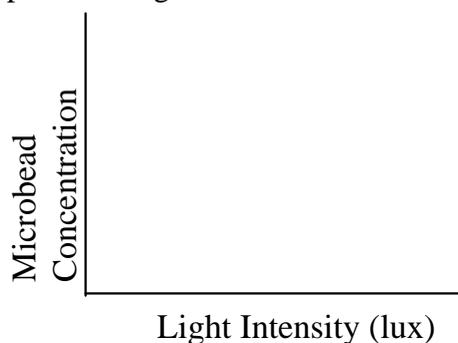
Investigation of Bacterial Transport Nano2Earth Activity Sheet

12. The known sample concentration is 4.5×10^8 beads/ml $\times 90$ ml/100ml = 4.05×10^8 beads/ml.
13. Measure the intensity of light as it passes from the flashlight through the beaker containing the known sample and into the light sensing probe. Collect light intensity for 10 continuous seconds. Record the average value.
14. Pour known sample of fluorescent microbead solution into column slowly.
15. Effluent will be collected in beaker labeled “unknown sample part 2”.
16. When approximately 100 ml of solution has collected in the beaker, remove the beaker from under the column and place in position to measure light intensity.
17. Collect light intensity for 10 continuous seconds. Record the average value.
18. Complete data table below:

	Clean Water	Known Sample	Unknown Sample from Part 1	Unknown Sample from Part 2
Light Intensity (lux)				
Microbead Concentration	0	4.05×10^8 beads/ml		

19. Using data table above, plot microbead concentration (Y axis) versus light intensity (X axis) for the clean water and known sample on a sheet of graph paper. See diagram 3.

Diagram 3. Example XY plot for calculating unknown sample concentration



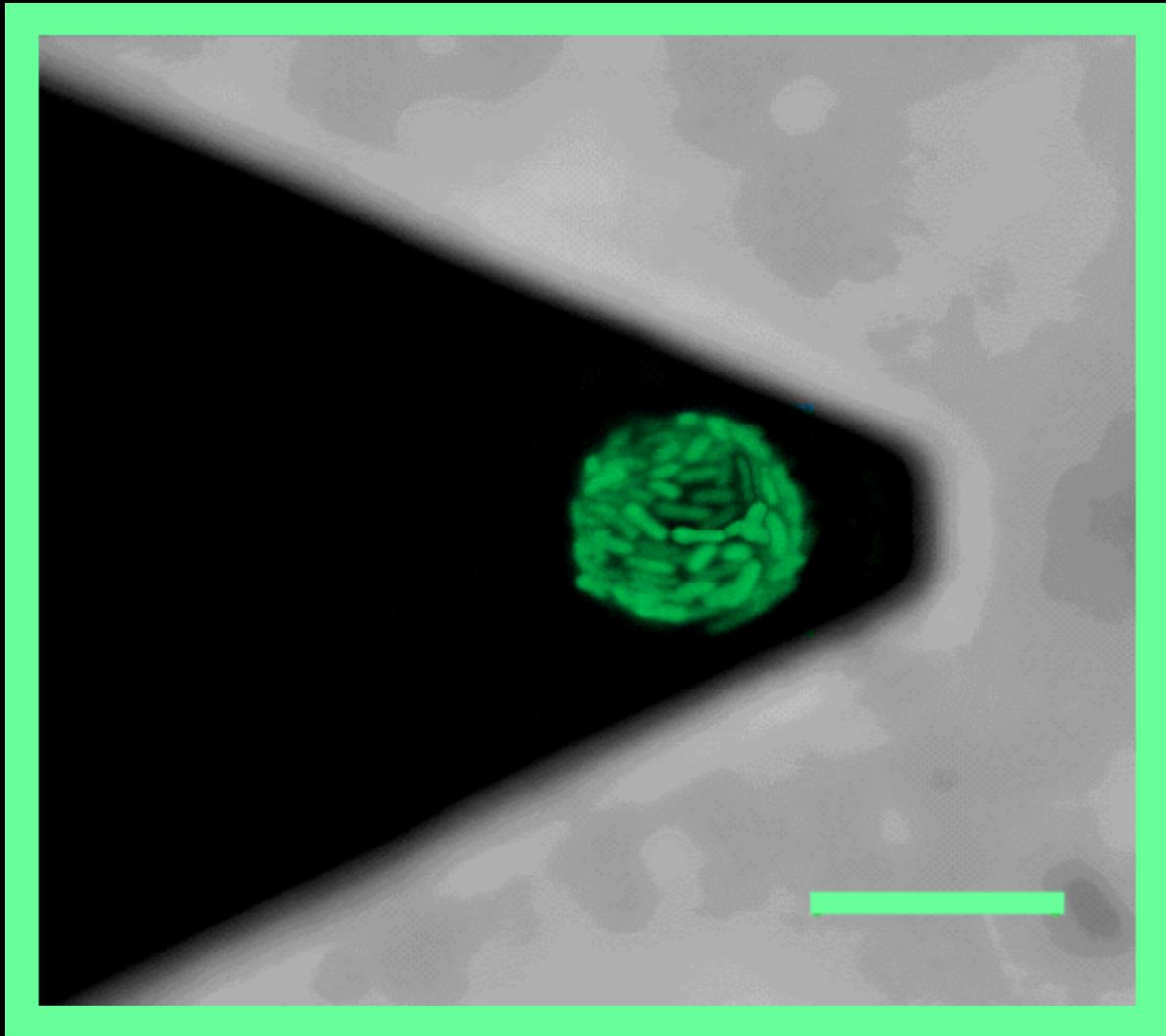
20. Draw a straight line between the two points on your graph. Label this line the absorption line.
21. On the X axis, find the light intensity value of your unknown sample from part 2.
22. Draw a vertical line from the X axis to the absorption line.
23. From the point on the absorption line, draw a horizontal line to the Y axis and determine the microbead concentration.

Investigation of Bacterial Transport

Nano2Earth Activity Sheet

Questions

1. Does adding 10 ml of HCl to the microbead solution raise or lower the pH?
2. What happens to the surface charges on the sand and microbead when pH is lowered? What happens to the surface charges when the pH is raised?
3. If you add a teaspoon of salt to the microbead solution, would you expect the surfaces to become more or less “sticky”?
4. Calculate the number of microbeads that remained in the column of sand.
5. Do you think live bacteria would behave differently than the microbeads? Why? *hint: are ALL bacteria the same size and shape?
6. Do you think sand accurately represents the rocks around your house and school?
7. List two differences between the sand column and the real rocks around your region.
8. When storms occur and flooding is evident, there are often concerns about drinking water purity. Why?
9. What would happen to the ionic strength of groundwater during a flood?



Confocal Laser Scanning Microscopy image of an Atomic Force Microscope (AFM) tip with a bacteria-coated bead attached. Scale bar is 2 microns, or 2000 nm. The bacteria are fluorescing green due to the presence of a special molecule that was genetically engineered.

Lesson 5

Nanoforces in Nature: Using Atomic Force Microscopy to Explore Mineral-Microbe Interactions

Purpose

If you did the Winogradsky column exercises, you learned that it has been proposed that bacteria are using iron minerals for respiration. The disappearance of the iron mineral is related to chemical or microbial reactions. It's possible that the microbes are using the iron mineral for respiration - they're "breathing" the mineral!

In the bacterial transport experiments, you saw that not all of the particles introduced to the column were transported through. Nanoscale interactions between the bacteria and the minerals in the sand were causing some of the bacteria to stick.

For either case, can the students think of any tools they can use from their lab to determine what is happening between the mineral and the bacteria? These interactions are occurring at an extremely small scale; at the nanoscale. We are going to have to use tools from nanotechnology in order to answer some of the questions. In this lesson, we will:

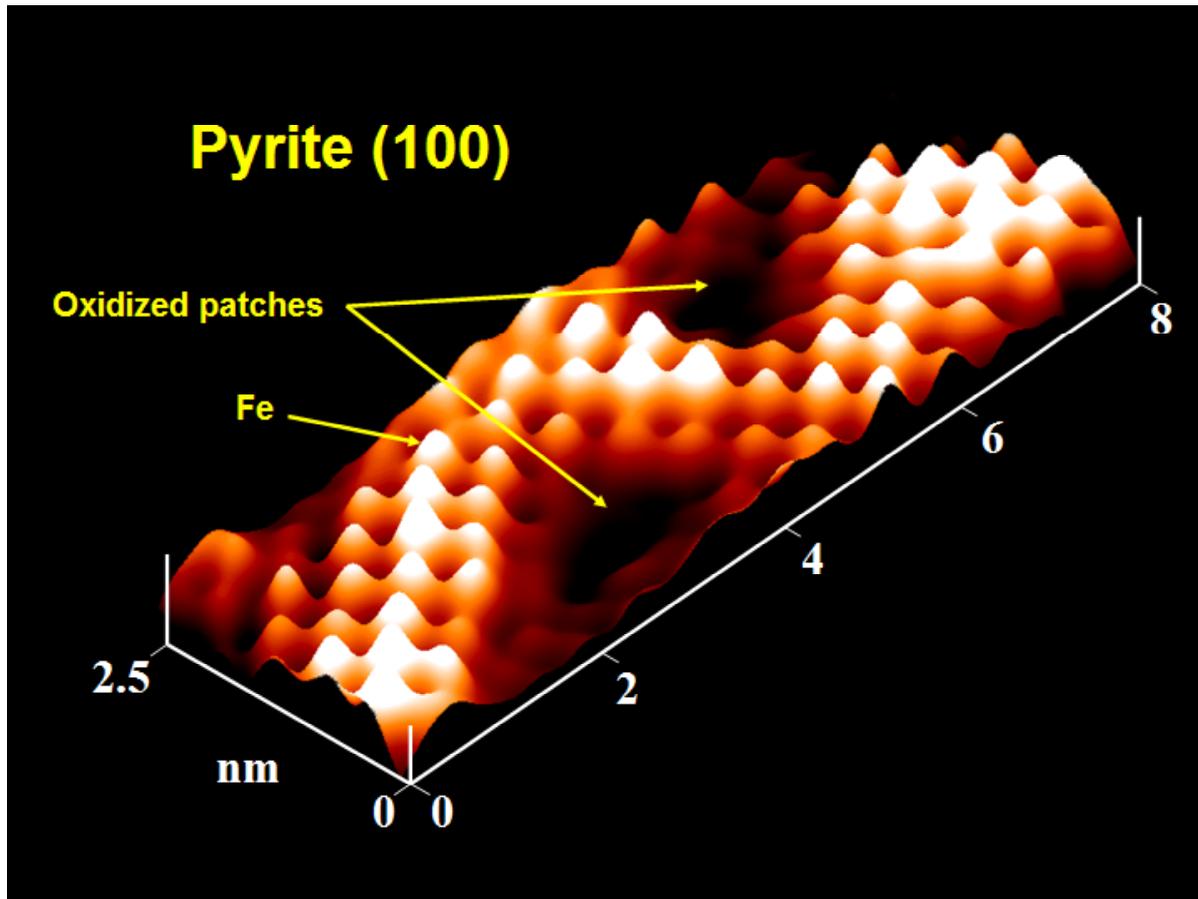
- Learn about the Atomic Force Microscope (AFM), one of the most important tools used in nanoscale science and technology
- See how the AFM is a versatile tool that can be used to study many things, including both organic and inorganic systems
- Discover how the AFM can be used to measure the forces of interaction between individual molecules, bacteria, and minerals
- Construct a model AFM
- Use the model AFM to generate data relating magnetic force to distance
- Plot actual research data collected from the AFM to generate a force curve
- Relate changes in AFM force curves to changing conditions in the column experiments
- Possible extension: Fit the data with a mathematical model; discuss the differences between a model and empirical data
- Possible extension: Integrate the force curves to look at the energies of interaction of the bacteria and minerals under different conditions

Background Information on Atomic Force Microscopy

The atomic force microscope is one of a family of instruments known as scanning probe microscopes. The first scanning probe technique, called Scanning Tunneling Microscopy (STM), was invented in 1982 by two scientists named Binnig and Rohrer at the IBM research labs in Zurich, Switzerland. In 1986, they received the Nobel Prize in physics for their invention. The STM works by taking a thin metal wire and treating it so a very sharp point is created. A conductive sample is placed in the instrument, and the metal wire is lowered toward the sample. When the wire and sample are less than one nanometer ($\ll 10$ Ångströms!) a phenomenon known as quantum mechanical tunneling will cause electrons to jump from the sample into the tip, or vice-versa. This generates a current. The amount of current varies exponentially as a function of the distance between the sample and tip; very tiny changes in the distance give large changes in the current. By scanning the tip across the surface and monitoring the current, an image of the surface can be obtained. Under many conditions, individual atoms on the surface can be imaged!

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The figure below shows an STM image of the mineral pyrite (FeS_2), an important mineral in environmental processes such as acid mine drainage. The bumps on the surface are individual iron atoms, and the “oxidized patches” are areas where the mineral has reacted in a similar way to how it would in the environment, generating acid. Research such as this helps us to understand the fundamental processes behind environmental problems...just exactly how does a pile of mine waste generate acid that wipes out all plant life and makes nearby water unpotable?



There are many limitations to the STM, such that it can be used only with samples that conduct electricity, and it is difficult to use with samples immersed in a solution (although it is somewhat possible). Binnig and Rohrer later invented the Atomic Force Microscope (AFM) to provide an alternative means to working with nonconductive and samples in water or other solutions. Instead of bringing a sharpened wire and a sample together, a spring system is used. A sharpened tip (typically made of silicon or silicon nitride) is attached to the bottom of a flexible cantilever. The tip is placed above the sample. A laser is bounced off the cantilever (above where the tip rests) and into a detector. As the two are brought together, forces exerted between the tip and sample cause the cantilever to bend upward (repulsive force) or downward (attractive force). The detector translates this motion of the laser into an electrical signal that is recorded on a computer.

With the AFM, images of a surface can be collected similar to the STM. However, the AFM can also be used to measure extremely small forces between small objects. Instead of scanning the cantilever/tip across the surface, it can be held in one place. Cycles of bringing the sample and tip together followed by pulling them apart in one location generate information known as force curves. Under some conditions, AFMs are capable of recording molecular or possibly atomic scale images, but also very importantly forces can be determined at the nano- and pico(10^{-12})-Newton level - approximately the force between two average people standing about 20 m apart.

Originally, a research-grade AFM system cost over \$100,000. They are continually becoming cheaper as more companies produce them and the demand increases.

National Standards

Nano2Earth Lessons	NSES Standards Addressed
Nanoforces in Nature	
Engage: Using The Atomic Force Microscope (AFM) to Study Microbe-Mineral Interactions Explore: What Happens When We Bring Bacteria and Minerals Together? Explain: Introduction to Force Curves Elaborate: Building a Model AFM Evaluate: Real-World Scenario	Unifying Concepts <ul style="list-style-type: none"> • Systems • Evidence • Models • Explanations • Changes • Measurement • Form and Function Science as Inquiry <ul style="list-style-type: none"> • Identify Questions and Concepts that Guide Scientific Explanations • Design and Conduct Scientific Investigations • Using Technology and Mathematics to Improve Investigations and Communications • Formulate and Revise Scientific Explanations and Models Using Logic and Evidence • Recognize and Analyze Alternative Explanations and Models • Understanding About Scientific Inquiry Physical Science <ul style="list-style-type: none"> • Structures and Properties of Matter • Motions and Forces Earth and Space Science <ul style="list-style-type: none"> • Geochemical Cycles Science and Technology <ul style="list-style-type: none"> • Understanding About Science and Technology Science in Personal and Social Perspectives <ul style="list-style-type: none"> • Natural Resources • Environmental Quality • Natural and Human Induced Hazards • Science and Technology in Local, National, and Global Challenges History and Nature of Science <ul style="list-style-type: none"> • Science as a Human Endeavor • Nature of Scientific Knowledge • Historical Perspectives

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Materials and Resources

Computer simulations are under development, and will be made optional. See page 86 for details.

Using AFM to Study Microbe-Mineral Interactions:

What Happens When We Bring Bacteria and Minerals Together

Building A Model AFM

Plotting and interpreting AFM Force Curve Data: various activity sheets, graphs, and data tables

Science Safety

The optional model AFM project requires the use of a laser pointer. Students should not shine the laser in each other's eyes.

Engage: Using the Atomic Force Microscope to Study Microbe-Mineral Interactions (Estimated time: 40 minutes)

1. Teachers should begin the lesson by asking students if they can think of any tools they can use to determine what is happening between the minerals and bacteria in the bacterial transport or Winogradsky column labs. Make a list of students' ideas on the board or overhead. Explain to the students that these interactions are occurring at an extremely small scale; at the nanoscale. We are going to have to use tools from nanotechnology in order to answer some of the questions. (5 minutes)
2. To learn more about nanoscience, teachers should read the background information contained in this lesson plan. This information may be shared with students to read, along with the handout: "Using AFM to Study Microbe-Mineral Interactions: Student's Introduction." (20 minutes)
3. After reading the background information, arrange the students in groups to discuss the readings. The students should write down their understandings of the articles and a list of questions they have about the AFM. (15 minutes)

Explore: What Happens When We Bring Bacteria and Minerals Together? (Estimated time: 40 minutes)

- Pass out the activity sheet: "What Happens When We Bring Bacteria and Minerals Together?" In their groups, students should examine the diagrams and discuss possible answers to the questions. (10 minutes)

In the second diagram, the cantilever bends downward in response to a repulsive force. It could be electrostatic, but it's not necessary to define what the type of force is. The important concept is that the cantilever bends upward and away from the mineral in response to a repulsive interaction. The third diagram shows the cantilever bending downward toward the mineral in response to an attractive force.

- Students should conduct the computer simulation "Introduction to Force Curves" following the accompanying student activity sheet. (30 minutes)

Activity sheet questions

1. What are the initial force and distance?

The initial force is zero and the distance is 140 nm. At 140 nm distance, the AFM does not measure any interaction between the bacteria and mineral.

2. At which distance does the interaction force become nonzero and is the initial force attractive or repulsive?

At approximately 40 nm, there is an initial repulsive force.

3. At some point, the bacteria will begin to snap down to touch the mineral. This is called the “jump to contact”. At which distance does this occur? Is this an attractive or repulsive interaction?

At approximately 15-20 nm separation distance, the force starts to become increasingly attractive along a linear trend. This is the signature of the jump to contact.

4. The mineral reaches its maximum height and the approach curve is completed. Now the retraction curve begins. Click the button marked “Begin retraction” and observe what happens. Does the bacteria pull away from the mineral at the same distance as the “jump to contact” on the approach curve (question 5)? What is happening?

No, the bacteria remains stuck to the mineral for some distance as the mineral retracts. A minimum force, called the adhesion force, must be overcome to separate them.

5. The maximum force between the bacteria and mineral, measured during the retraction curve, is known as the **adhesion force**. What is the adhesion force between the bacteria and mineral in this simulation? Is it attractive or repulsive?

The adhesion force is approximately 0.2 nN, and it is always attractive. Although the force on the graph is -0.2 nN, the absolute value is used when discussing the adhesion force.

Explain: Force Curve Computer Simulations (Estimated time: 40 minutes)

- Students should explore how force curves can be collected with various bacteria, minerals, and solutions using the computer simulation “Force curves 2 – going further” and accompanying worksheet. (40 minutes)

Bacteria	Mineral	Solution pH	Initial interaction (attractive or repulsive)	Jump to contact distance (nm)	Adhesion force (nN)
A	quartz	7	repulsive	18	0.20
B	quartz	7	repulsive	25	0.32
A	quartz	4	repulsive	15	0.35
B	quartz	4	attractive	50	0.54
A	iron oxide	7	attractive	40	0.39
B	iron oxide	7	attractive	30	0.43
A	iron oxide	4	attractive	15	0.31
B	iron oxide	4	repulsive	20	0.58

A Note About the Computer Simulations...

Nano2Earth is an evolving project, and we thank you for your participation and interest. The computer simulations are currently in a state of development and/or improvement. The simulations are designed to help the teachers and students visualize physically what is happening in the Atomic Force Microscope (AFM) as a force curve is collected. Although this visualization is helpful to understand and interpret the force curves, the simulations are not required for this lesson. Alternatively, the force curves can be generated and explored by students using the provided graphs and data tables. When using the simulations, the provided graphs and data tables are not necessary.

Check our website (www.nanoed.vt.edu) for computer simulation updates.

Activity Sheet Questions

- Often, the type of initial interaction can be related to the electrostatic forces between the bacteria and mineral. Given that quartz is negatively charged for solution pH >2, what are the charges (positive or negative) of Bacteria A, Bacteria B, and the iron oxide mineral at pH 4 and 7? Use information from the preceding table to help you.

At pH 4, Bacteria A are negatively charged. Bacteria B and the iron oxide are positively charged. At pH 7, Bacteria A and Bacteria B are negatively charged. Iron oxide is positively charged.

- If Bacteria A were transported through sediment containing quartz and iron oxide, to which mineral is it more likely to adhere? Is it more likely to adhere at pH 4 or 7?

Bacteria A are more likely to adhere to iron oxide than quartz due to the sign of the initial interaction. The bacteria are more likely to adhere at pH 4; the jump to contact distance is much greater.

- Bacteria B are disease-causing (pathogenic) bacteria that are adhered to sediments where your drinking water is supplied. You can drill a well and inject a solution to flush the bacteria. Should you use pH 4 or pH 7 water?

This question addresses the adhesion force. Larger adhesion forces imply the bacteria are more strongly adhered. Thus, pH 7 water should be used to flush out the bacteria because the adhesion force is lower in magnitude (a less negative number) with both quartz and iron oxide than with either of them at pH 4.

Elaborate: Building a Model AFM (Estimated time: 20-70 minutes)

- To extend their understandings of the Atomic Force Microscope (AFM), students may be constructing a model of the AFM using the “Model AFM Activity Sheet.” This may be done in collaboration with the Industrial Arts Department. (20 minutes)
- (optional) Students should finish building and experiment with the model AFM and follow the instructions on the “Model AFM Activity Sheet” to generate a force curve. Students should also compare the model AFM with the actual AFM as described in previous handouts and diagrams of the AFM cantilever. (50 minutes)

Evaluate: Real-World Scenarios (Estimated time: 20-70 minutes)

The scenarios are designed to correspond to concepts and problems encountered in Lessons 3 and 4. If your class completed the Winogradsky column labs (Lesson 3), the appropriate scenario is “Arsenic Poisoning in Bangladesh”. If you completed the bacterial transport labs (Lesson 4), have your class try the “Bacterial Transport” scenario.

These scenarios use data that was actually collected in the NanoGeoscience and Technology Laboratory in the Department of Geosciences at Virginia Tech, although their application to these problems is simulated. The data are currently in the process of integration into computer simulations that are very similar to those seen by the students in the earlier sections of Lesson 5.

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Introduction to Force Curves-Arsenic Poisoning in Bangladesh Scenario

1. Look at the retraction curves under aerobic conditions. Remember, the negative numbers represent an attractive force. Which mineral do the bacteria stick to more, the iron oxide or the aluminum oxide? Do the bacteria have a purpose or advantage associated with this stronger attraction?

The bacteria adhere more strongly to the aluminum oxide under aerobic conditions. An advantage is not clear; consider any reasonable answers. This is an example of where science has not yet provided a definitive reason.

2. Look at the retraction curves under anaerobic conditions. Which mineral do the bacteria stick to more? Use information from the graphs to support your conclusions.

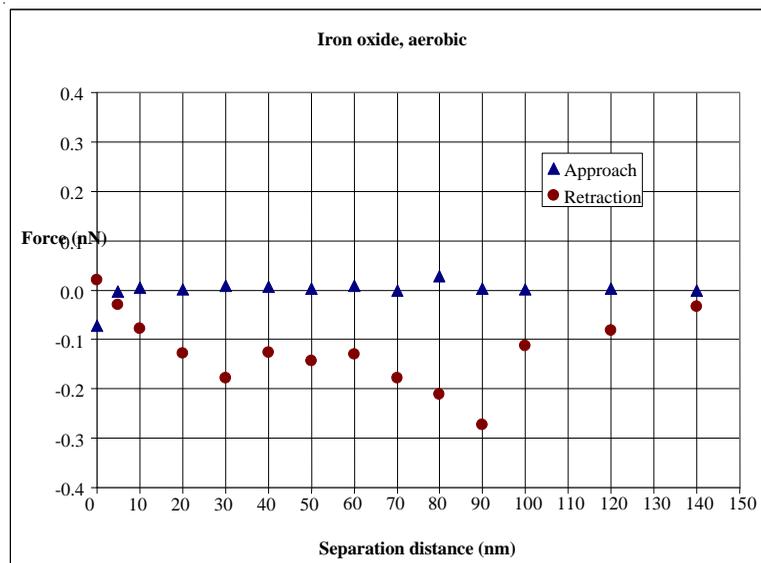
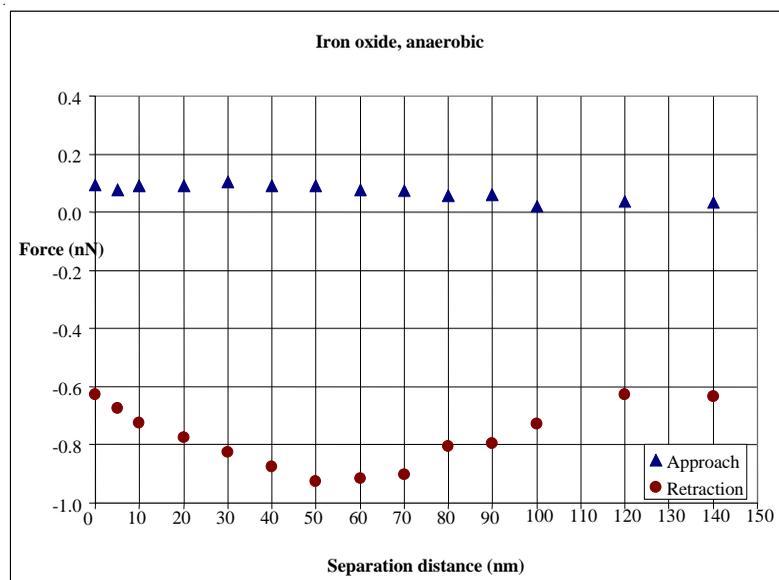
The bacteria adhere more strongly to the iron oxide mineral under aerobic conditions, as can be determined by the adhesion force values.

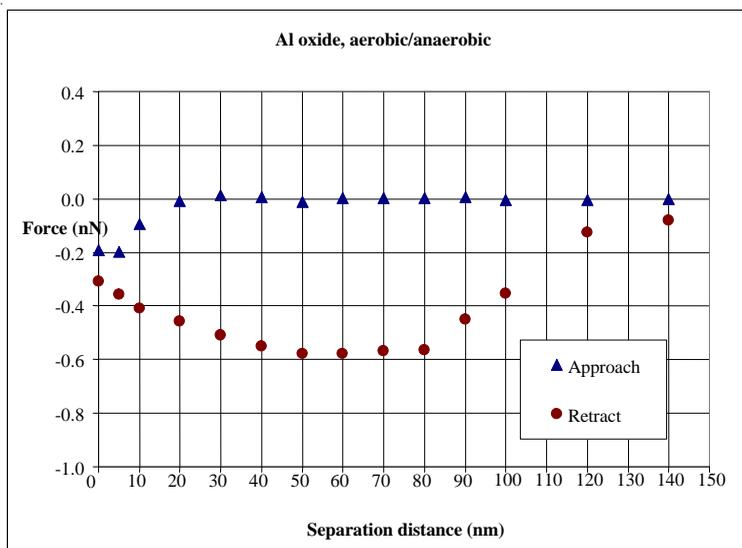
3. The curve for aluminum oxide was identical when comparing aerobic and anaerobic bacteria. Is there significance to this effect? What, if any, is the significance?

The bacteria cannot use the aluminum oxide mineral for respiration, so the lack of oxygen will not trigger an attraction. There is no advantage for the bacteria to be attached to the aluminum oxide under aerobic vs. anaerobic conditions.

4. Under which conditions do the bacteria have the strongest interaction with the iron oxides? Do they have a purpose or advantage with this attraction?

The bacteria have the strongest interactions with the iron oxide under anaerobic conditions. This is an example of an adaptation to survive; attaching to the iron oxide allows them to respire anaerobically.





5. Which environmental conditions could lead to release of arsenic resulting in higher levels of arsenic contamination in the wells? Are there any ways to avoid these environmental conditions?

The arsenic is likely released during anaerobic conditions as the iron oxide minerals are reduced. Students might suggest ways to eliminate anaerobic conditions, such as removal of standing water or pumping of oxygen into the groundwater. However, these solutions are not practical due to the widespread distribution of arsenic throughout such a large area. The arsenic contamination problem still exists today.

Scenario: Bacterial Transport in Groundwater Scenario

1. What are the potential sources of the *E. coli*?

The most likely sources of E. coli are sewer line leakage/overflow or transport from animal fecal matter into the water source areas for the town. E. coli live in the gastrointestinal tracts of the animals (as they do with humans).

2. Based on this information, can you now be more specific about the source of contamination?

Improvements in the sewer line seemed to solve the problem, indicating that the sewer line was the source of the problem.

3. Based on the bacterial transport column experiments, what do you hypothesize caused the release of bacteria to groundwater?

A change in the chemistry of the water after the rainstorms caused bacteria that previously had been adsorbed in the agricultural fields to be transported instead.

Simulation 1 - Ionic strength. Note: if access to the computer simulation is available, the graphs can be alternatively generated using the data table at the end of the student exercise.

4. At what approximate distance does the approach curve move away from zero? Is the initial force repulsive or attractive?

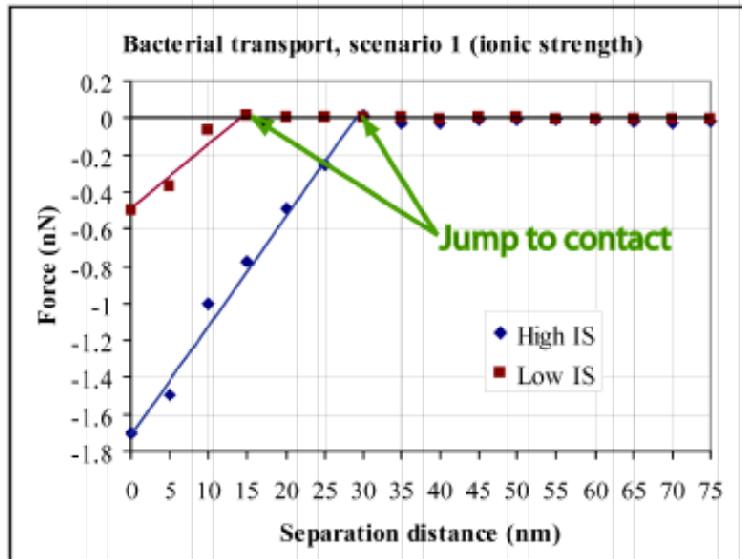
The approach curves are significantly different from zero for the high and low ionic strength cases at approximately 25 nm and 10 nm, respectively. In both cases, the initial force is attractive. The convention is that a negative force indicates an attractive interaction.

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5. At what approximate distance is the “jump to contact” shown in the approach curves?

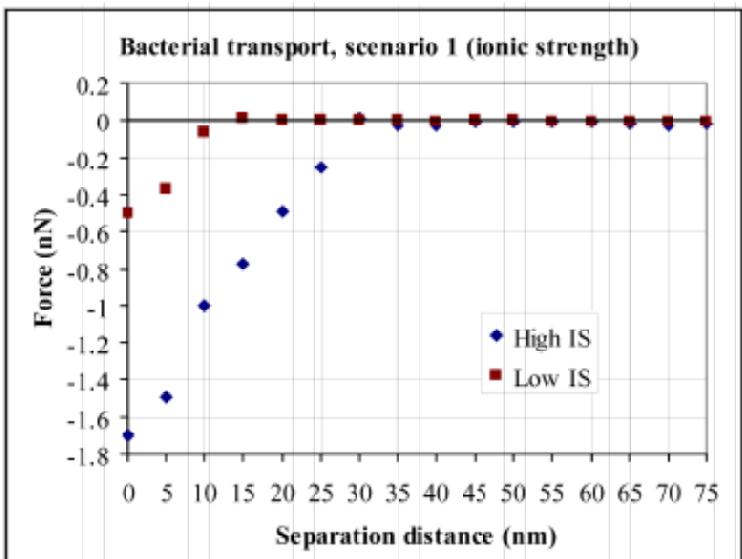
The jump to contact is used operationally here to describe the point at which the force between the surface and tip/bacteria begins to snap down together. This is observed as a linear trend toward increasingly attractive as the separation distance decreases. The diagram to the right illustrates how this can be determined for simulation 1.

The jump to contact distances for the high and low ionic strength cases are 30 nm and 15 nm, respectively.



6. What does the difference in “jump to contact” distances tell you about the difference in interaction between *E. coli* and the mineral at these two values of ionic strength?

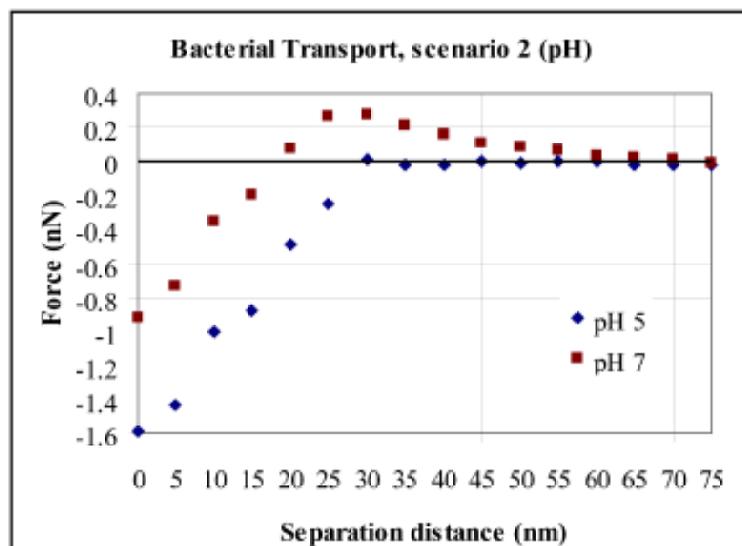
*The *E. coli* are much more likely to stick to the minerals in the sediment at high ionic strength than low ionic strength. Although there are attractive interactions at both ionic strengths, the attractive interactions occur at much larger separation distances at high ionic strength.*



Simulation 2 - pH

7. For each value of pH, at what approximate distance does the approach curve move away from zero? Is the initial force repulsive or attractive?

At pH 7, the curve indicates a repulsive interaction at approximately 55 nm separation distance. At pH 5, the first interaction is attractive, which occurs at approximately 25 nm separation distance.



8. Is the repulsive force greater at pH 5 or pH 7?

The repulsive force is much greater at pH 7.

9. Based on your answers to the questions above, would you predict that the bacteria adhere (stick) to the surfaces better at pH 5 or pH 7? Does this agree with what you observed in the bacterial transport column experiments?

At pH 7, the curve indicates a repulsive interaction at approximately 55 nm separation distance. At pH 5, the first interaction is attractive, which occurs at approximately 25 nm separation distance. This is likely to have been the same result as the column experiments if relatively pure quartz/silica sand was used.

10. Based on the sticking coefficient data, do bacteria stick to surfaces better at lower or at higher pH? Why? Does this answer agree with the AFM data?

A higher sticking efficiency indicates the bacteria are more sticky, so they appear to stick to the sediment better at lower pH. This must have to do with the type of minerals in the sediments. Based on the previous exercises, this is consistent with the sediment having a significant amount of quartz. Quartz and E. Coli have strong negative surface charges at pH 7, but are less strongly negative at pH 5 where there are more protons in the solution to screen the charge. This does agree with the AFM data.

11. Do bacteria stick to surfaces better at lower or higher ionic strength? Why? Does your answer agree with the AFM data?

The bacteria stick to surfaces better at higher ionic strength. There are more ions in solution to screen the opposing charges. This is in agreement with the AFM data.

12. Which affects the sticking efficiency of bacteria more: ionic strength or pH?

The solution pH seems to have a stronger effect than ionic strength.

13. If you were the town engineer, could you prevent the contamination problem from reoccurring? If so, what would you do?

There may be many possible ways to improve the situation. One way may be to try and coat the sediment with iron oxide, which has a positive surface charge at neutral pH, or build structures that prevent water from seeping through animal pens and into the town's water supply areas.

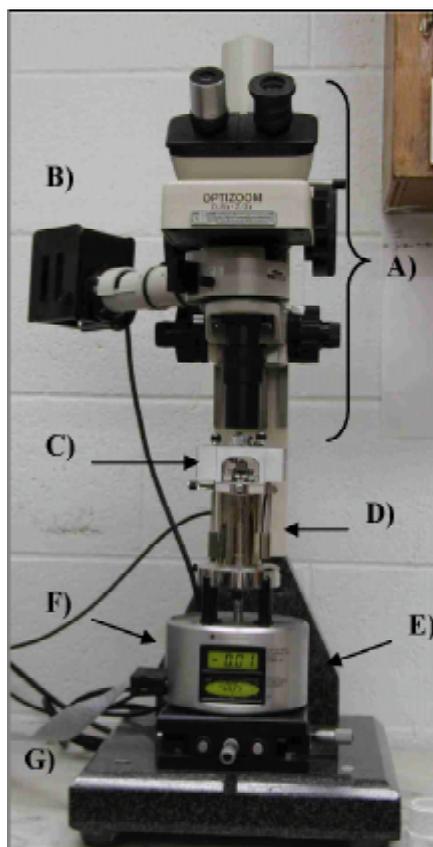
Nanoforces in Nature

Nano2Earth Activity Sheet

Using the Atomic Force Microscope (AFM) to Study Microbe-Mineral Interactions

The Atomic Force Microscope is a very versatile instrument that has been extremely important in the development of nanoscale science and technology. It allows people to manipulate objects at a nanometer scale. One nanometer is extremely small; a typical human hair is approximately 60,000 nm across! Individual atoms are about 0.1 nm across; one water molecule has dimensions of about 0.3 nm. The AFM is capable of measuring nanoNewton forces (10^{-9} N)! How much is a nanoNewton? Imagine that you are sitting at a desk looking at a computer monitor. One nanoNewton is approximately the same amount as the gravitational force between you and a computer monitor sitting in front of you!

The AFM is so effective in part because it uses a very sensitive spring system called a cantilever. The cantilever is similar to a miniaturized plastic ruler. It is small enough and flexible enough that it will bend upward or downward in response to very small forces. At the end of the cantilever is a small sharp tip. A sample is placed on the microscope, underneath the cantilever's tip. As the sample and the cantilever are brought together, the forces of interaction between the sample and tip push the end of the cantilever up or down. The forces are recorded.



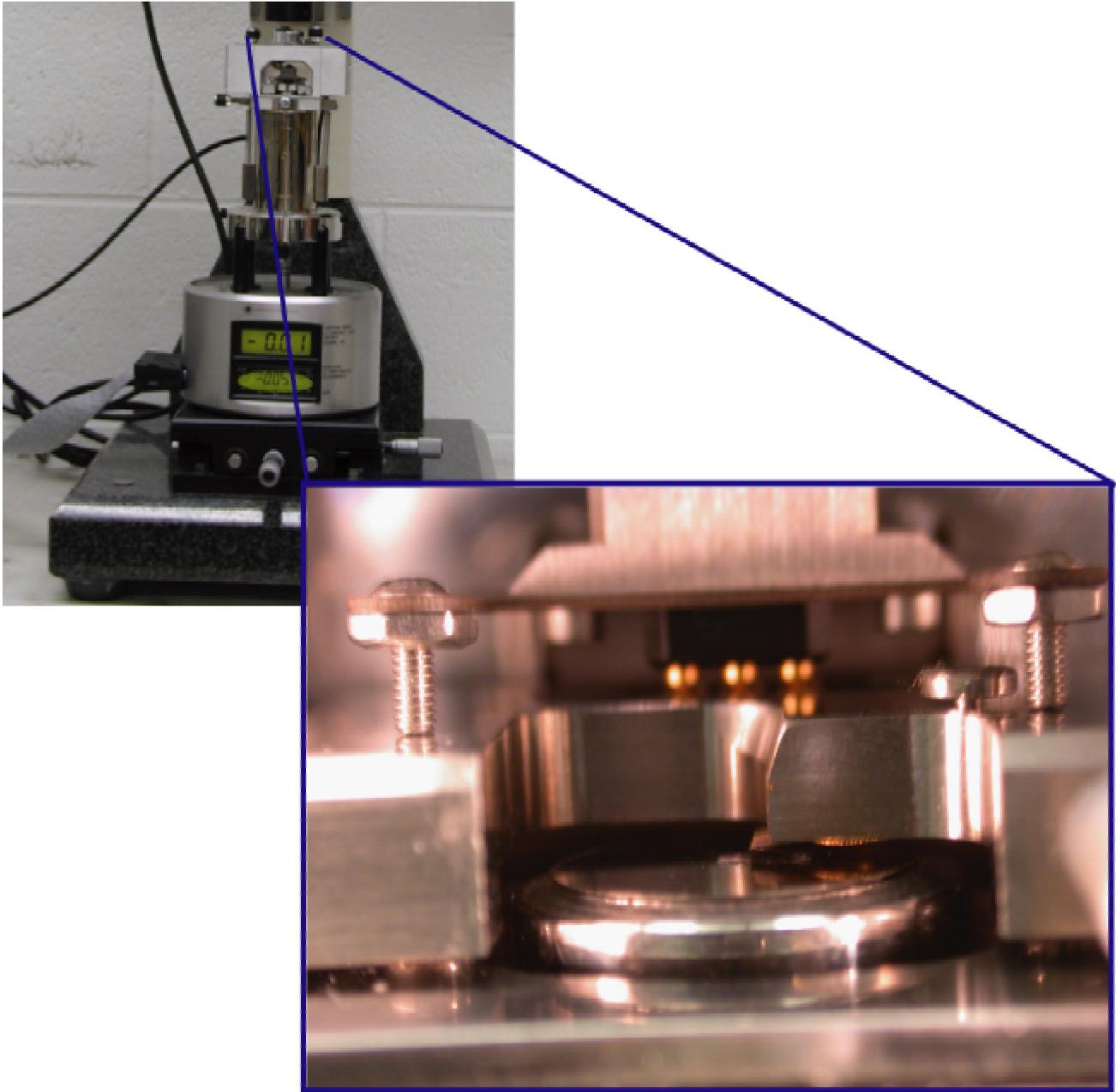
A picture of a typical AFM is shown to the left. The parts are:

- A) Optical microscope. The user needs this to see if the sample and cantilever are in the proper arrangement.
- B) Light source for the optical microscope.
- C) Called the “head”, this is where the sample and cantilever go. Pictures on the next page show enlarged views of this area.
- D) Called the “scanner”, this device moves the sample up and down (or sideways). The amount of movement can be controlled with an accuracy of less than one nanometer.
- E) The silver electronics unit has displays that assist the operator.
- F) A cable is attached just below the arrow. This cable connects the AFM to a set of electronics that form an interface between the microscope and a computer.
- G) AFMs usually are operated on a specially designed table to reduce the amount of vibration felt by the microscope.



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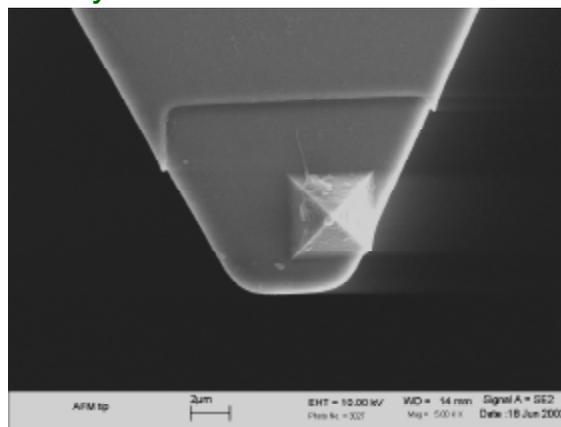
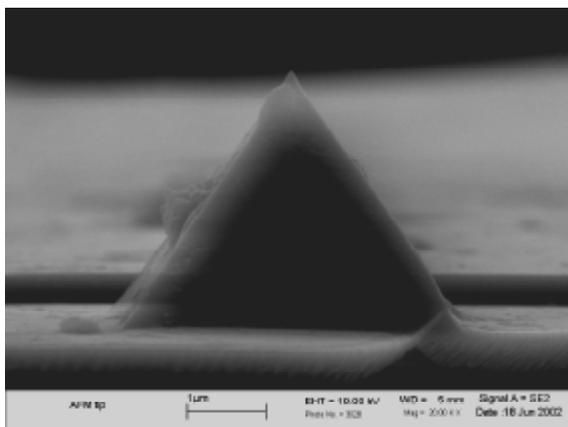
Nano2Earth Activity Sheet



In the two pictures above, you can see the AFM from the previous picture, with an enlarged image of where the sample sits. The sample sits on top of the scanner, the device that moves the sample closer and farther away from the tip. On the inset, you can see labeled the cantilever, sample, and the top of the scanner where the sample rests.

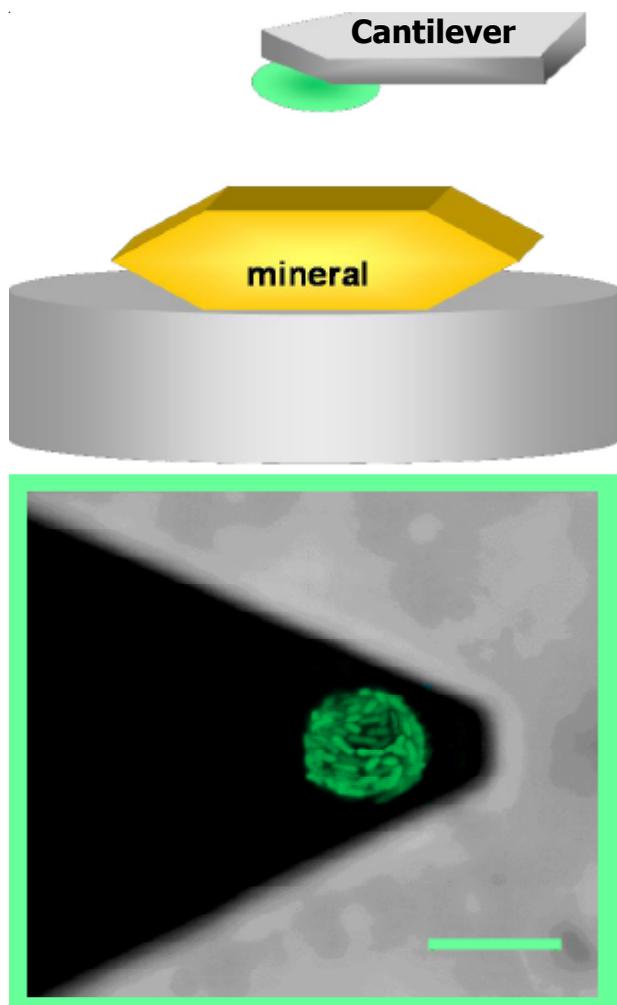
Normally, a sharp tip that looks like an upside-down pyramid resides on the underside of the cantilever. Often, the tip is replaced with other things. For example, if the goal is to measure the force of interaction between bacteria and a mineral, the bacteria can be attached to the cantilever and lowered down toward the mineral. Sometimes a bead is first attached to the cantilever, and then the bacteria are attached to the bead.

Nanoforces in Nature Nano2Earth Activity Sheet



Two scanning electron micrographs of AFM tips on the end of triangular-shaped cantilevers are shown above. The tip is shaped like a triangular pyramid. Notice the scale bars are one micron (left) and two microns (right). A micron is 10^{-6} m, or 1000 nm. Notice also how the tip is not centered on the cantilever; this is due to an error in the manufacturing process.

The experiment may look like the following: A glass bead coated with bacteria is attached to the bottom of the cantilever. The bacteria-covered bead on the end of the cantilever is put into the AFM and aligned above a mineral sample. An aqueous solution is injected into the AFM to make sure the bacteria stay alive during the experiment. The solution can be changed at any time to run experiments with variations in



parameters such as dissolved oxygen, pH, or other solutes.

The bottom picture shows the bacteria-coated bead at the end of an AFM cantilever. The view is of the bottom side; it's upside-down. The bacteria remain attached to the bead because they're linked to it with a special molecule. They're fluorescing brightly here in response to a laser beam. The scale bar is 10 microns.

The tip (or bacteria-coated bead) and sample can be brought together and pulled apart by a computer-controlled device. With the addition of a laser and a detector, it's possible to determine the forces of interaction between the tip (or bacteria-coated bead) and the mineral. The laser is bounced off the top of the cantilever into the detector. Any motion of the cantilever will cause the laser to be displaced in the detector.

Since the cantilever can be considered a spring, the displacement of the laser beam in the detector can be converted to a force using Hooke's Law, where

$$\text{Force} = kx$$

The spring constant k reflects the rigidity of the cantilever, and x is the displacement of the laser.

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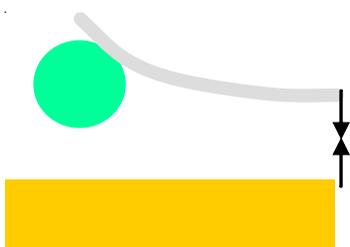
Nano2Earth Activity Sheet

What Happens When We Bring Bacteria and Minerals Together?



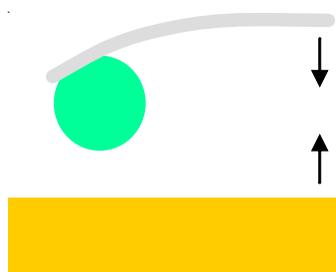
mineral

Looking at the cantilever and bacteria-covered bead from the side, you'll see something like this.

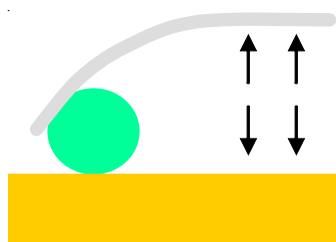


As the bacteria-covered bead is lowered, the spring may deflect upward as shown in the picture to the left.

What is causing it to deflect upward?



Now let's consider some other examples. In this case, what if as the bead and sample are brought together, the cantilever bends downward. How would you characterize this interaction?



Eventually, regardless of what happened initially as the bead and sample were brought together, they will stick. They will remain stuck until the force that holds them together, the adhesion force, is overcome.

Nanoforces in Nature

Nano2Earth Activity Sheet

Introduction to Force Curves - Using Computer Simulation

In the previous worksheet, you learned about what types of interactions may occur as bacteria (or bead) and mineral are brought together and then pulled apart. Scientists use the Atomic Force Microscope to measure the forces of interaction by measuring what's known as a **force curve**. If the spring constant of the cantilever is known, one cycle of bringing the bacteria and mineral together then pulling them apart generates a graph of force vs. distance known as a force curve. This activity simulates a force curve between Bacteria A and the mineral quartz in a solution with pH 7.

Force curves have two main parts, the **approach curve** (bringing the bacteria and mineral together) and the **retraction curve** (pulling them apart). The approach curve tells us how the bacteria and mineral attract and/or repel each other, as they get closer. The retraction curve can be used to determine how strongly the bacteria and mineral stick together, a quantity called the **adhesion force**.

- Load the simulation “Introduction to Force Curves” by loading the Nano2Earth CD and choosing the “run simulations” option. On the next screen, click on the “Introduction to Force Curves” button.
 - You will see a simulation with two panels. The left-hand side is a diagram of the AFM. The force curve, a graph of interaction force vs. distance will be displayed on the right-hand side. Notice that the force is given on the y-axis and the distance on the x-axis. Notice that zero on the x-axis scale represents the bacteria and mineral first touching, while large numbers represent when they are farther apart. Click on the “start simulation” button.
1. What are the initial force and distance (when the separation is the greatest)?
 2. At which distance does the interaction force become nonzero, and is the initial force at that point attractive or repulsive?
 3. At some point, the bacteria will snap down to touch the mineral. This is called the “jump to contact”. At which distance does this occur? Is this an attractive or repulsive interaction?
 4. The mineral reaches its maximum height and the approach curve is completed. Now the retraction curve begins. Click the button marked “Begin retraction” and observe what happens. Does the bacteria pull away from the mineral at the same distance as the “jump to contact” on the approach curve (question 5)? What is happening?
 5. The maximum force between the bacteria and mineral, measured during the retraction curve, is known as the **adhesion force**. What is the adhesion force between the bacteria and mineral in this simulation? Is it attractive or repulsive?

Nanoforces in Nature

Nano2Earth Activity Sheet

Introduction to Force Curves -Without Computer Simulation

In the previous worksheet, you learned about what types of interactions may occur as bacteria (or bead) and mineral are brought together and then pulled apart. Scientists use the Atomic Force Microscope to measure the forces of interaction by measuring what's known as a **force curve**. If the spring constant of the cantilever is known, one cycle of bringing the bacteria and mineral together then pulling them apart generates a graph of force vs. distance known as a force curve. This activity simulates a force curve between Bacteria A and the mineral quartz in a solution with pH 7.

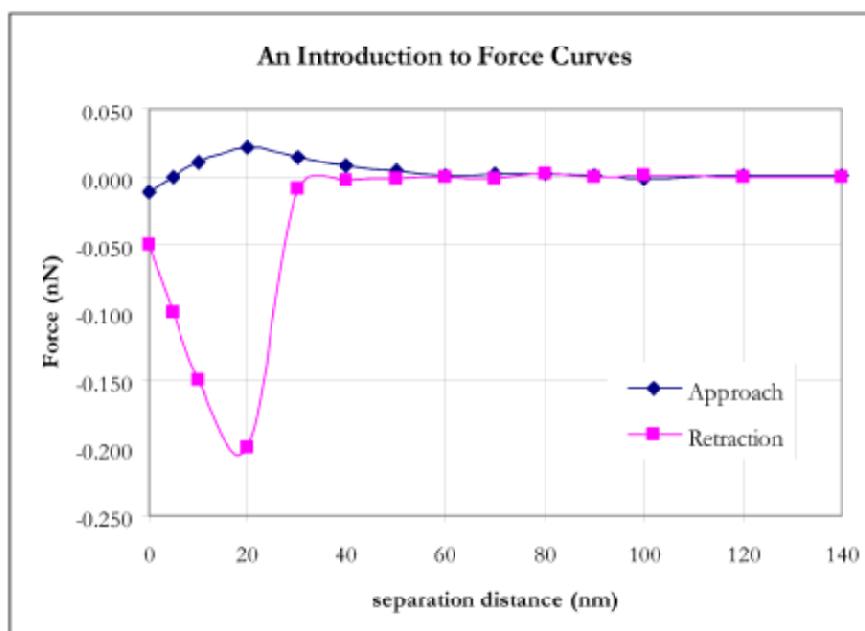
Force curves have two main parts, the **approach curve** (bringing the bacteria and mineral together) and the **retraction curve** (pulling them apart). The approach curve tells us how the bacteria and mineral attract and/or repel each other, as they get closer. The retraction curve can be used to determine how strongly the bacteria and mineral stick together, a quantity called the **adhesion force**.

- Study the graph on the next page (handout). This is a force curve, a graph of interaction force vs. distance between a bacteria (called Bacteria A) and a mineral (quartz, SiO_2). Notice that the force is given on the y-axis and the distance on the x-axis. Notice that zero on the x-axis scale represents the bacteria and mineral first touching, while large numbers represent when they are farther apart.
1. What are the initial force and distance (when the separation is the greatest)?
 2. Looking at the approach curve data, at which distance does the interaction force become nonzero and at that point is the initial force attractive or repulsive?
 3. At some point, the bacteria will snap down to touch the mineral. This is called the “jump to contact”. At which distance does this occur? You can tell because the approach curve just starts to turn slope downwards on the graph. Is this an attractive or repulsive interaction?
 4. The mineral reaches its maximum height and the approach curve is completed. Now the retraction curve begins. Study the retraction curve data. Does the bacteria pull away from the mineral at the same distance as the “jump to contact” on the approach curve (question 5)? What is happening?
 5. The maximum force between the bacteria and mineral, measured during the retraction curve, is known as the **adhesion force**. What is the adhesion force between the bacteria and mineral? Is it attractive or repulsive?

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*Force Curve Data Table for
Introduction to Force Curves Activity*

d (nm)	Approach Force (nN)	Retract Force (nN)	d(nm)	Approach Force (nN)	Retract Force (nN)
140	0.001	0.000	50	0.005	-0.001
120	0.001	0.000	40	0.009	-0.003
100	-0.001	0.001	30	0.015	-0.009
90	0.001	0.000	20	0.022	-0.200
80	0.002	0.002	10	0.011	-0.150
70	0.003	-0.001	5	0.000	-0.100
60	0.001	0.000	0	-0.011	-0.050



Nanoforces in Nature

Nano2Earth Activity Sheet

Building a Model AFM

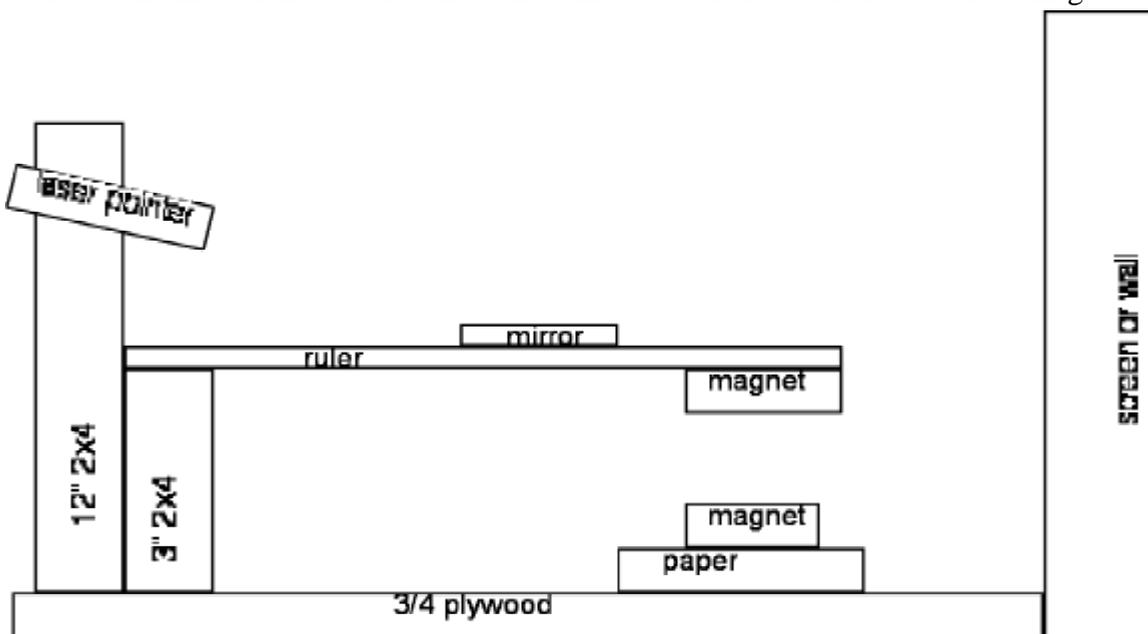
This is a procedure to construct a simple model that demonstrates how an AFM operates. It is important to understand that this is only a model. The magnets in this model are representations. The top magnet represents the AFM tip. Sometimes, a bacteria cell is glued onto this tip. The bottom magnet represents a mineral surface. The forces at work in an AFM are not actually magnetic.

Materials

3/4 inch plywood, 18" x 18"	small mirror
2x4, 12" long	laser pointer
2x4, 3" long	screws or nails
plastic or metal ruler (must bend)	tape
2 magnets	

Procedure

Use nails, screws, and/or tape to attach the materials according to the following diagram. The laser pointer must be oriented so that the laser will bounce off the mirror and hit a screen or wall. The point of the laser must be marked on the screen/wall when the model has no interaction between the magnets.



Stacking additional paper under the magnet will raise the magnet and decrease the distance between the magnets. As the magnets are moved closer, there will be a force interaction, which bends the ruler. If the force is attractive, the ruler will bend down, and the dot on the wall will move down. If the force is repulsive, the opposite will occur, and the ruler will bend up and the dot will move up. A stronger force will move the dot more. The force is proportional to the change in distance. The x-axis on a force curve is distance. This distance is represented by the distance between the magnets. The y-axis on a force curve is force. This force is represented by the displacement of the laser dot on the wall. Movement upward represents a positive force. Movement downward represents a negative force.

Going further challenge: Create a force curve that displays magnetic force vs. distance using the model.

Nanoforces in Nature Nano2Earth Activity Sheet

Force Curves 2 - Going Further - With Computer Simulation

In this computer simulation and activity, you will investigate how changing the type of bacteria, mineral, or solution pH can affect the force curves.

- Begin the simulation “Force Curves 2” by loading the Nano2Earth CD and choosing the “run simulations” option. On the next screen, click on the “Force Curves 2” button.
- The simulation begins with the force curve you investigated in the previous activity between Bacteria A and the mineral quartz in a solution with pH 7. In this simulation, you will be able to change the type of bacteria, the mineral, and the solution pH.

Bacteria	Mineral	Solution pH	Initial interaction (attractive or repulsive)	Jump to contact distance (nm)	Adhesion force (nN)
A	quartz	7			
B	quartz	7			
A	quartz	4			
B	quartz	4			
A	iron oxide	7			
B	iron oxide	7			
A	iron oxide	4			
B	iron oxide	4			

1. Often, the type of initial interaction can be related to the electrostatic forces between the bacteria and mineral. Given that quartz is negatively charged for solution pH >2, what are the charges (positive or negative) of Bacteria A, Bacteria B, and the iron oxide mineral at pH 4 and 7? Use information from the table above to help you.
2. If Bacteria A were transported through sediment containing quartz and iron oxide, to which mineral is it more likely to adhere? Is it more likely to adhere at pH 4 or 7?
3. Bacteria B are disease-causing (pathogenic) bacteria that are adhered to sediments where your drinking water is supplied. You can drill a well and inject a solution to flush out the bacteria. Should you use pH 4 or pH 7 water?

Nanoforces in Nature Nano2Earth Activity Sheet

Force Curves 2 - Going Further - Without Computer Simulation

In this activity, you will investigate how changing the type of bacteria, mineral, or solution pH can affect the force curves.

- Use the following data tables and graphs to fill in the chart below. These are force curve data collected between two different species of bacteria (Bacteria A and Bacteria B), two different minerals that are very common in soils and sediments (quartz and iron oxide), and two different solution pH values (4 and 7).

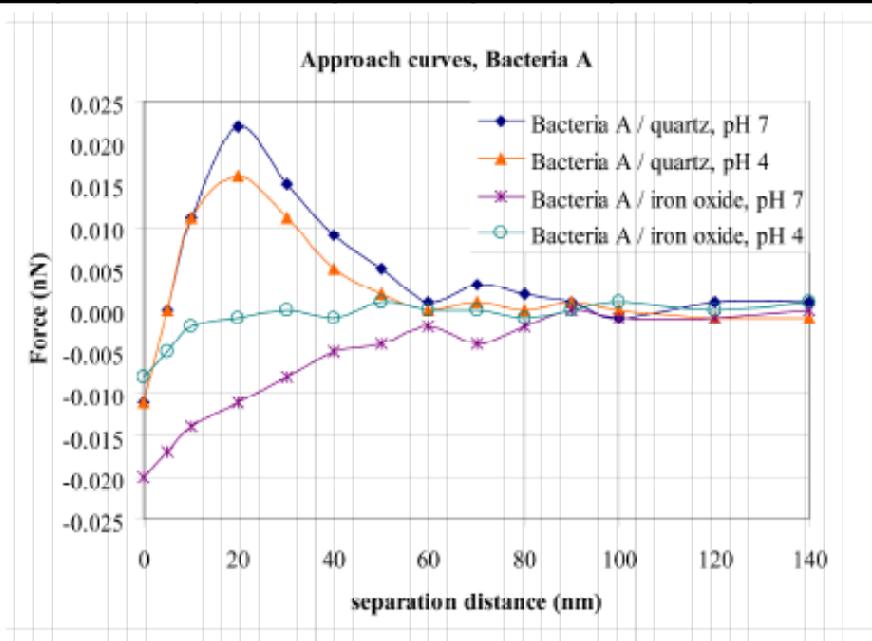
Bacteria	Mineral	Solution pH	Initial interaction (attractive or repulsive)	Jump to contact distance (nm)	Adhesion force (nN)
A	quartz	7			
B	quartz	7			
A	quartz	4			
B	quartz	4			
A	iron oxide	7			
B	iron oxide	7			
A	iron oxide	4			
B	iron oxide	4			

- Often, the type of initial interaction can be related to the electrostatic forces between the bacteria and mineral. Given that quartz is negatively charged for solution pH >2, what are the charges (positive or negative) of Bacteria A, Bacteria B, and the iron oxide mineral at pH 4 and 7? Use information from the table above to help you.
- If Bacteria A were transported through sediment containing quartz and iron oxide, to which mineral is it more likely to adhere? Is it more likely to adhere at pH 4 or 7?
- Bacteria B are disease-causing (pathogenic) bacteria that are adhered to sediments where your drinking water is supplied. You can drill a well and inject a solution to flush out the bacteria. Should you use pH 4 or pH 7 water?

Nanoforces in Nature Nano2Earth Activity Sheet

Approach Curve Data Table for Force Curves 2 - Going Further Activity

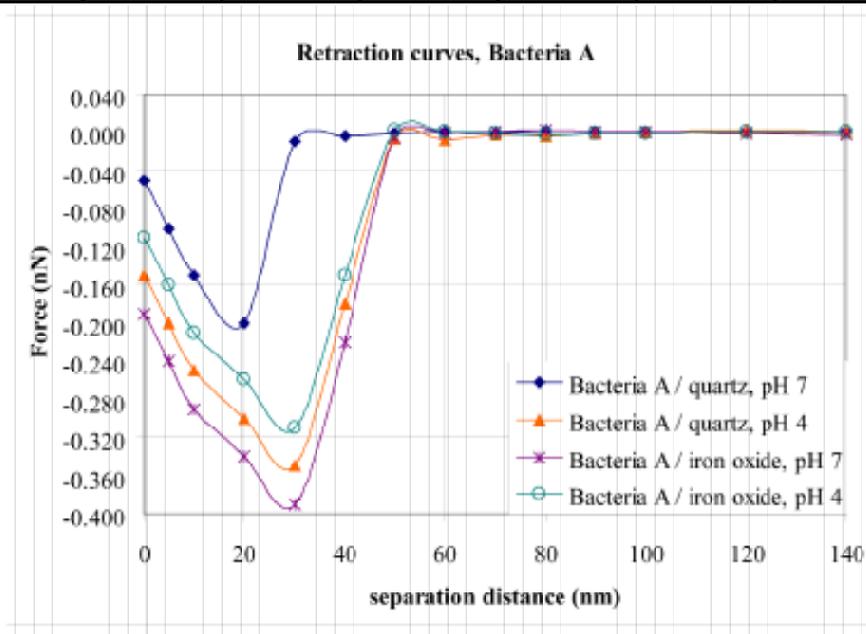
Bacteria:	A	B	A	B	A	B	A	B
Mineral:	quartz	quartz	quartz	quartz	iron oxide	iron oxide	iron oxide	iron oxide
d (nm)	pH 7	pH 7	pH 4	pH 4	pH 7	pH 7	pH 4	pH 4
140	0.001	0.000	-0.001	-0.001	0.000	-0.001	0.001	0.001
120	0.001	-0.001	-0.001	-0.002	-0.001	-0.002	0.000	-0.001
100	-0.001	0.000	0.000	-0.001	-0.001	-0.002	0.001	0.000
90	0.001	-0.002	0.001	0.001	0.000	0.000	0.000	0.002
80	0.002	-0.001	0.000	0.000	-0.002	0.001	-0.001	0.001
70	0.003	0.000	0.001	-0.001	-0.004	-0.002	0.000	0.003
60	0.001	0.001	0.000	-0.003	-0.002	-0.004	0.000	0.001
50	0.005	0.002	0.002	-0.002	-0.004	-0.001	0.001	0.003
40	0.009	0.008	0.005	-0.004	-0.005	-0.004	-0.001	0.005
30	0.015	0.012	0.011	-0.006	-0.008	-0.003	0.000	0.004
20	0.022	0.005	0.016	-0.010	-0.011	-0.006	-0.001	0.006
10	0.011	-0.001	0.011	-0.013	-0.014	-0.009	-0.002	0.000
5	0.000	-0.005	0.000	-0.015	-0.017	-0.012	-0.005	-0.003
0	-0.011	-0.016	-0.011	-0.018	-0.020	-0.015	-0.008	-0.006



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*Retraction Curve Data Table for
Force Curves 2 - Going Further Activity*

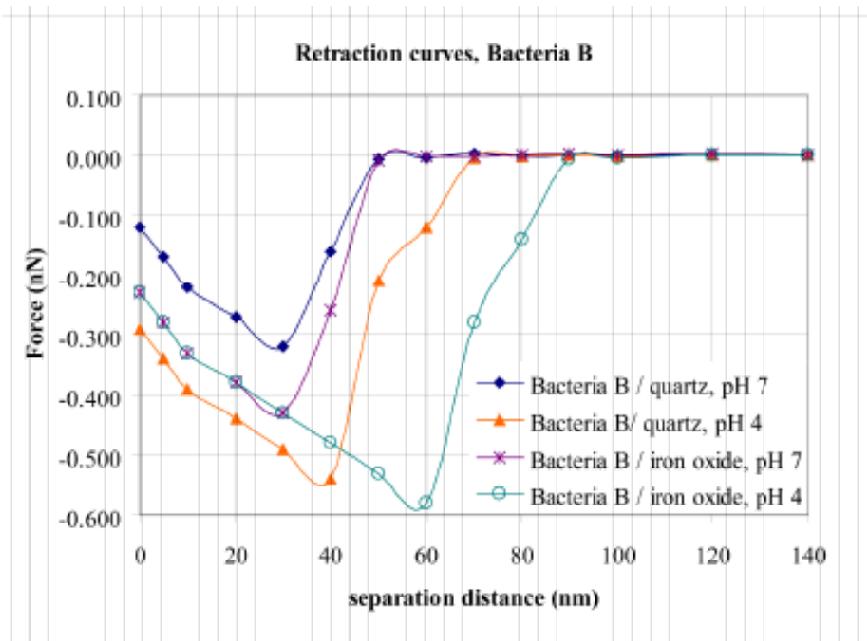
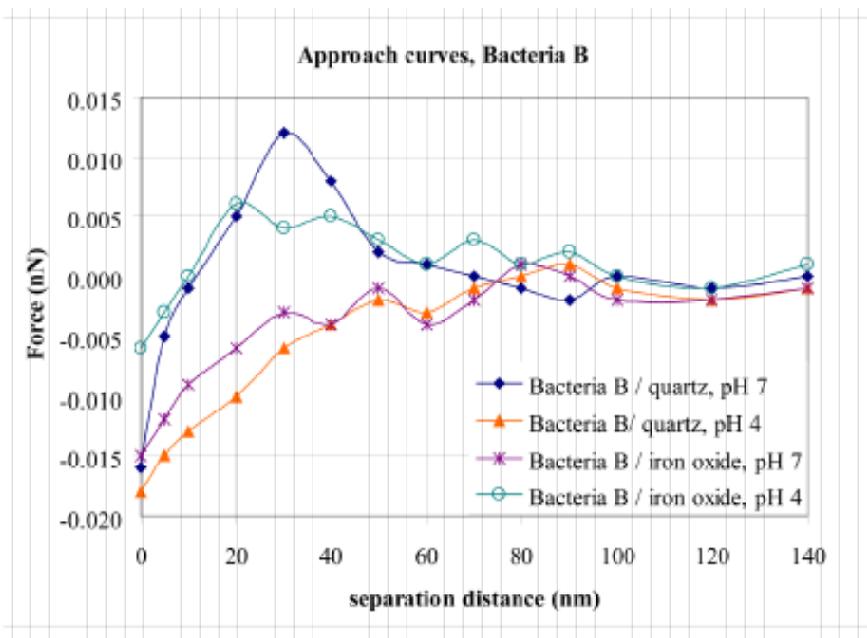
Bacteria:	A	B	A	B	A	B	A	B
Mineral:	quartz	quartz	quartz	quartz	iron oxide	iron oxide	iron oxide	iron oxide
d (nm)	pH 7	pH 7	pH 4	pH 4	pH 7	pH 7	pH 4	pH 4
140	0.000	-0.001	0.000	-0.001	-0.002	-0.001	0.000	-0.001
120	0.000	0.000	0.002	-0.001	-0.001	0.001	0.000	0.000
100	0.001	-0.001	0.001	-0.003	0.001	0.000	-0.001	-0.005
90	0.000	0.000	-0.001	-0.001	0.000	0.001	-0.001	-0.007
80	0.002	-0.002	-0.003	-0.002	0.002	0.000	-0.002	-0.140
70	-0.001	0.001	-0.002	-0.004	0.001	-0.003	-0.001	-0.280
60	0.000	-0.005	-0.008	-0.120	-0.001	-0.002	0.001	-0.580
50	-0.001	-0.008	-0.006	-0.210	-0.005	-0.009	0.002	-0.530
40	-0.003	-0.160	-0.180	-0.540	-0.220	-0.260	-0.150	-0.480
30	-0.009	-0.320	-0.350	-0.490	-0.390	-0.430	-0.310	-0.430
20	-0.200	-0.270	-0.300	-0.440	-0.340	-0.380	-0.260	-0.380
10	-0.150	-0.220	-0.250	-0.390	-0.290	-0.330	-0.210	-0.330
5	-0.100	-0.170	-0.200	-0.340	-0.240	-0.280	-0.160	-0.280
0	-0.050	-0.120	-0.150	-0.290	-0.190	-0.230	-0.110	-0.230



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Graphs for Force Curves 2 - Going Further Activity



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Real-World Scenario: Arsenic Poisoning in Bangladesh

Read the following summary of a problem with arsenic in the groundwater in Bangladesh. Then consider the scenario presented to you. What answers do you have for the scenario questions?

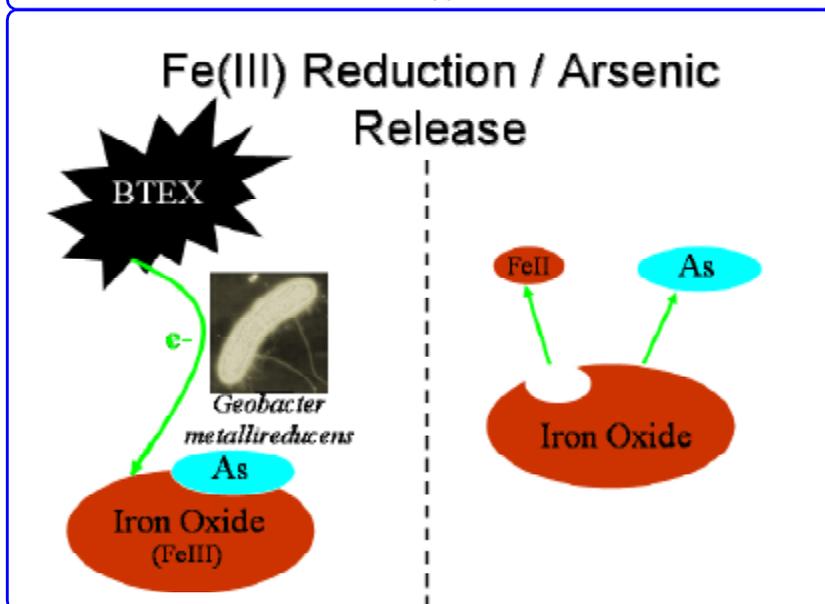
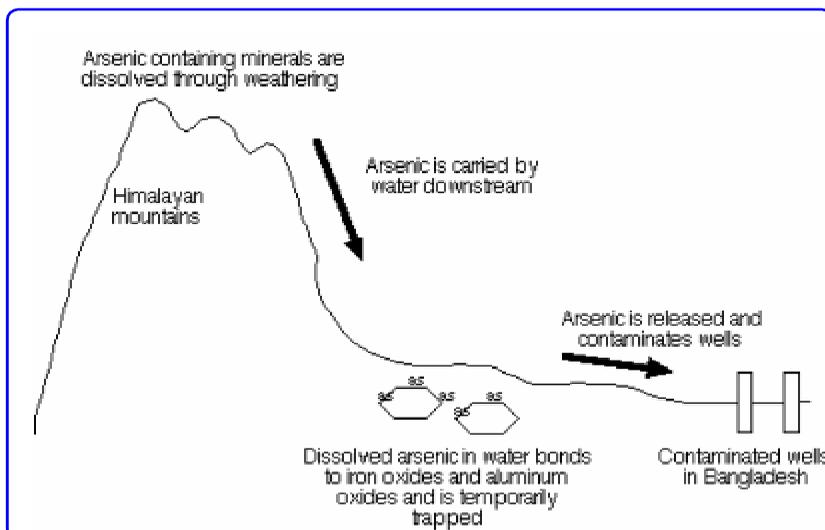
The Water Quality Problem in Bangladesh

Levels of arsenic in the groundwater in Bangladesh have been measured above the World Health Organization maximum of 10 parts per billion. This means that over 35 million Bangladeshis drink water from their wells that are contaminated with arsenic. This is a serious problem because arsenic has been linked to cardiovascular and neurological diseases and is a human carcinogen.

In Bangladesh, the groundwater filters through ground that was once an ancient river delta system. The sediments that made up the river delta system contain aluminum oxides, iron oxides, and organic carbon. In the rocks of the Himalayas, mountains which surround Bangladesh, minerals can be found that contain arsenic. As the Himalayas erode due to weathering, the rocks release the arsenic which is carried down rivers and streams and eventually finds its way into the sediments. Certain minerals in the sediments, the aluminum and iron oxides, are extremely efficient at removing arsenic from the water by trapping it on the surface through adsorption. This is shown in the diagram.

One current theory that addresses how the arsenic got into the groundwater and wells considers the role played by the iron oxides.

Some scientists think that the iron oxides (that have arsenic attached to their surfaces) in the groundwater are being dissolved because the bacteria is reducing the iron from iron (III) to iron (II). When the iron oxide dissolves, it releases the arsenic into the water. As long as the iron oxides are undissolved, they hold the arsenic to their surfaces. Once they dissolve, however, the arsenic is also released into the water environment. Another hypothesis is that there is a change in the solution conditions that releases the arsenic mainly from the aluminum oxide



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You are a scientist trying to investigate the source of the arsenic contamination in the drinking water. Your job is to come up with a way of testing one or more of the hypotheses presented above.

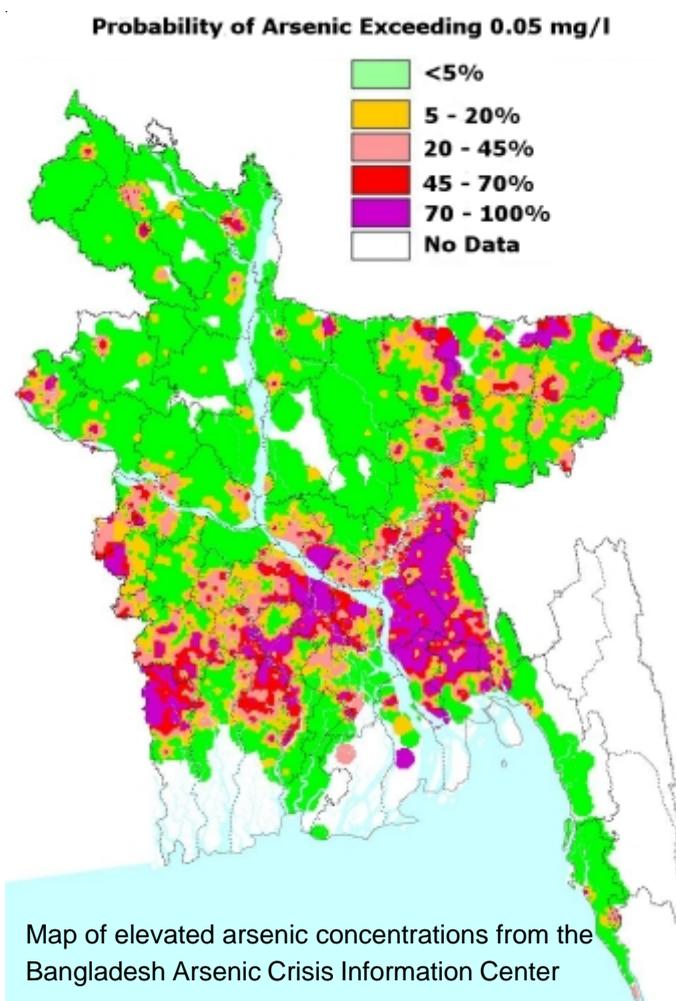
What did you conclude from the Winogradsky column about the disappearance of the red/orange color during the experiment?

In order to relate the interactions between the bacteria and minerals in the sediments of Bangladesh and the changes that you have observed in the Winogradsky column, you have collected samples of bacteria and mineral oxides from the sediments. Next, you will collect data and create AFM force curves for 4 combinations of your samples:

1. bacteria and iron oxide mineral; aerobic conditions
2. bacteria and iron oxide mineral; anaerobic conditions
- 3 and 4 bacteria and aluminum oxide mineral; aerobic and anaerobic conditions

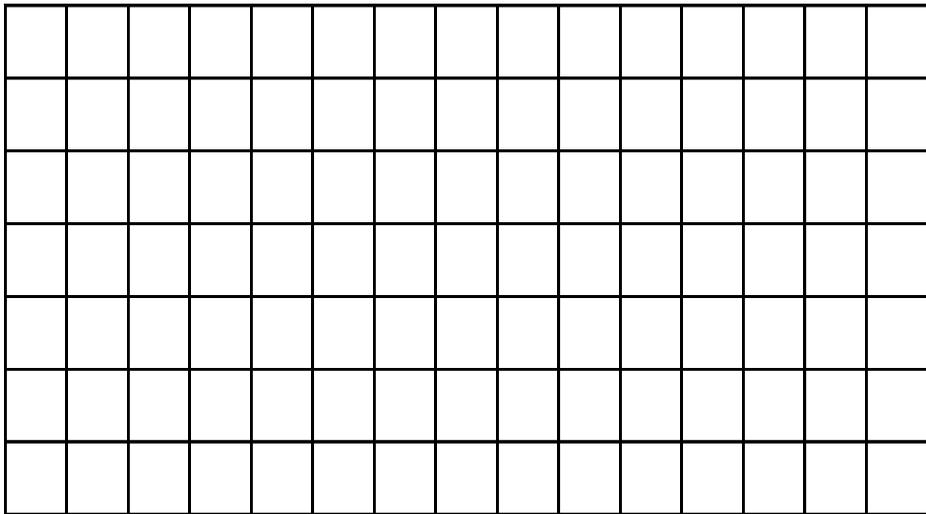
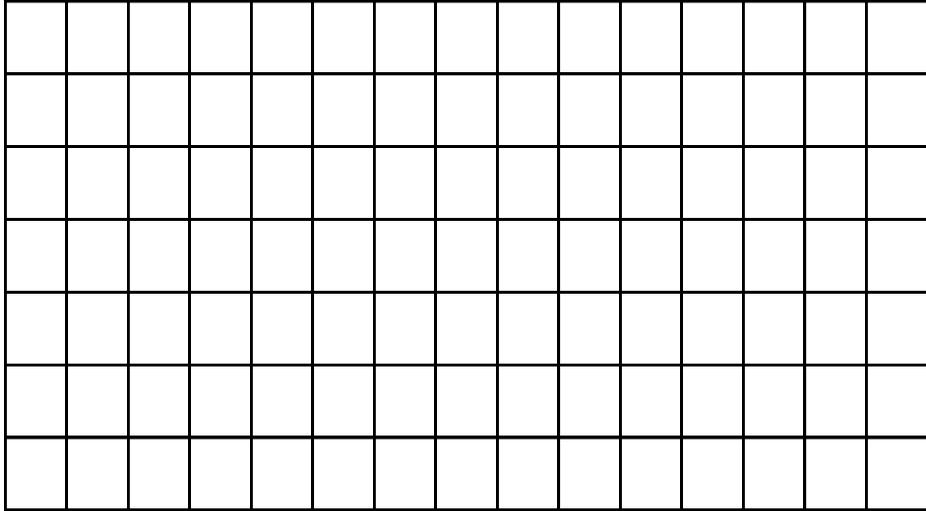
This data will be generated using the computer simulation “Arsenic in Groundwater.” These are actual data adapted from a scientific study published in the journal *Science*. The results of experiments 3 and 4 were nearly identical, and are not reported separately.

- Begin by labeling each of the three graphs provided with one of the three experiment titles above. Put the graphs of the two iron oxide experiments on the same page. Put the aluminum oxide graph on the other page.
- Label the axes – on the x-axis, “separation distance in nanometers”, and on the y-axis, “Force in nanoNewtons”. If you wish, you may use the abbreviations nm for nanometer and nN for nanoNewton.
- Fill in the x-axis and y-axis scale. For the x-axis, label the graph from 0 nm on the left to 150 nm on the right. Fill in the intermediate values, 10 nm for each step. For the y-axis, label the bottom –1.0 nN and the top 0.4 nN. Fill in the intermediate values in 0.2 nN steps.
- Start the “Arsenic in Groundwater” simulation. Plot the force/distance data for each set of conditions.



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Plotting Force Curves for Bangladesh Scenario



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Question sheet: Comparing Force Curves

1. Look at the retraction curves under aerobic conditions. Remember, the negative numbers represent an attractive force. Which mineral do the bacteria stick to more, the iron oxide or the aluminum oxide? Do the bacteria have a purpose or an advantage associated with this stronger attraction?
2. Look at the retraction curves under anaerobic conditions. Which mineral do the bacteria stick to more? Use information from the graphs to support your conclusions.
3. The curve for aluminum oxide was identical when comparing aerobic and anaerobic bacteria. Is there significance to this effect? What, if any, is the significance?
4. Under which conditions do the bacteria have the strongest interaction with the iron oxides? Do they have a purpose or an advantage with this attraction?
5. Which environmental conditions could lead to release of arsenic resulting in higher levels of arsenic contamination in the wells? Are there any ways to avoid these environmental conditions?

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Force Curve Data Table for Bangladesh Scenario

	iron oxide: anaerobic	iron oxide: anaerobic	iron oxide: aerobic	iron oxide: aerobic	Al oxide: aerobic/ anaerobic	Al oxide: aerobic/ anaerobic
d (nm)	approach	retract	approach	retract	approach	retract
140	0.033	-0.633	-0.001	-0.033	-0.001	-0.082
120	0.039	-0.628	0.002	-0.081	-0.003	-0.125
100	0.020	-0.728	0.001	-0.113	-0.005	-0.353
90	0.060	-0.795	0.003	-0.272	0.005	-0.450
80	0.058	-0.806	0.027	-0.211	0.003	-0.564
70	0.075	-0.902	0.000	-0.179	0.001	-0.567
60	0.078	-0.915	0.008	-0.130	0.003	-0.577
50	0.090	-0.926	0.003	-0.144	-0.013	-0.578
40	0.092	-0.876	0.006	-0.126	0.007	-0.552
30	0.103	-0.826	0.008	-0.179	0.012	-0.508
20	0.092	-0.776	0.001	-0.129	-0.009	-0.458
10	0.090	-0.726	0.005	-0.079	-0.095	-0.408
5	0.078	-0.676	-0.002	-0.029	-0.198	-0.358
0	0.093	-0.626	-0.072	0.021	-0.192	-0.308

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Scenario: Bacterial Transport in Groundwater

You live in a town located in an agricultural area. The area's economy is based on animal industry, including dairy and beef cattle, as well as poultry. The town's drinking water is supplied by one well and they have a small sewer line. Recently, a large subdivision was constructed in the town, but no additional wells or sewer lines were constructed to service the subdivision.

Soon after people move into the subdivision, many people in the town report stomach illnesses. The town engineer decides to analyze the well water for contamination; results show that the water contains *E. Coli*, a pathogenic bacteria found in fecal matter.

1. What are the potential sources of the *E. Coli*?

To prevent further contamination, the town upgrades the sewer line. After this, there are no additional reports of stomach illnesses.

2. Based on this information, can you now be more specific about the source of contamination?

The following summer, the town is hit with several large rainstorms, which dilute the groundwater. Soon after the storms, people begin to get sick again. Analysis of the water again shows contamination with *E. Coli*. The engineer is perplexed, as he thought he had fixed their problem by upgrading the sewer line.

3. Based on the bacterial transport column experiments, what do you hypothesize caused the release of bacteria to groundwater?

The engineer asks a scientist at a local university to help figure out the problem. The scientist collects some sediment samples from the aquifer, and isolates the *E. Coli* from the sediment. She runs several AFM experiments to see how the bacteria attach to the sediment. She then conducts the experiments at different values of pH and different values of ionic strength to see if either of these would change the way that the bacteria attach to the surfaces. Results for two experiments, one conducted with low ionic strength (diluted groundwater collected after rainstorm) and the other conducted with high ionic strength (normal groundwater collected before rainstorm) are shown in the **Computer Simulation 1: Ionic strength**. Use the simulations and the following instructions to prepare your own force curves from the scientist's data.

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- Begin by labeling the following two graphs with either “Low Ionic Strength: IS = 0.005” or “High Ionic Strength: IS=0.05”
- Label the axes – on the x-axis, “separation distance in nanometers”, and on the y-axis, “Force in nanoNewtons”. If you wish, you may use the abbreviations nm for nanometer and nN for nanoNewton.
- Fill in the x-axis and y-axis scales. For the x-axis, label the graph from 0 nm on the left to 75 nm on the right. Fill in the intermediate values, 5 nm for each step. For the y-axis, label the bottom - 1.8 nN and the top 0.2 nN. Fill in the intermediate values in 0.2 nN steps.
- For each 5 nm of separation distance, use the Computer Simulation to pick the value of the force, and plot these below.

Questions, simulation 1:

4. At what approximate distance does the approach curve move away from zero? Is the initial force repulsive or attractive?
5. At what approximate distance is the “jump to contact” shown in the approach curves?
6. What does this difference in “jump to contact” distance tell you about the difference in interaction between *E. coli* and the mineral at these two values of ionic strength?

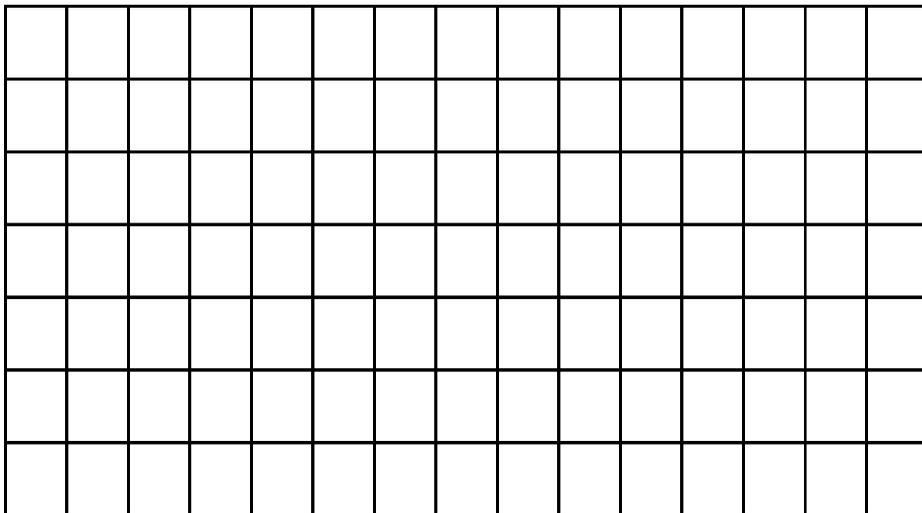
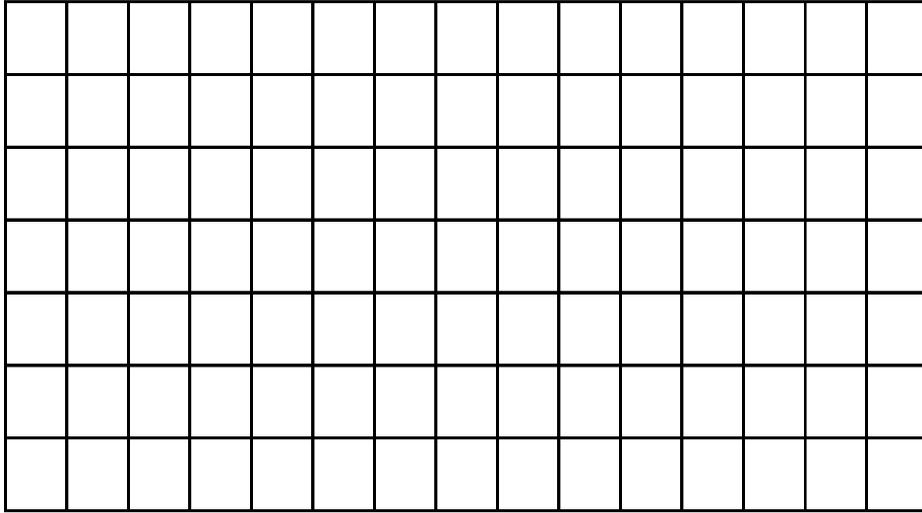
The scientist then runs some experiments varying the pH of the groundwater and then measuring the forces between the *E. coli* and the mineral surface using the AFM. Results are shown in **Computer Simulation 2: pH**.

Again, prepare your own force curves from the simulation data.

- Begin by labeling the two graphs provided below with either “pH 5” or “pH 7”.
- Label the axes – on the x-axis, “separation distance in nanometers”, and on the y-axis, “Force in nanoNewtons”.
- Fill in the x-axis and y-axis scales. For the x-axis, label the graph from 0 nm on the left to 75 nm on the right. Fill in the intermediate values, 5 nm for each step. For the y-axis, label the bottom -1.6 nN and the top 0.4 nN. Fill in the intermediate values in 0.2 nN steps.
- For each 5 nm of separation distance, use the results from **Computer Simulation 2: pH** to pick the value of the force, and plot these below.

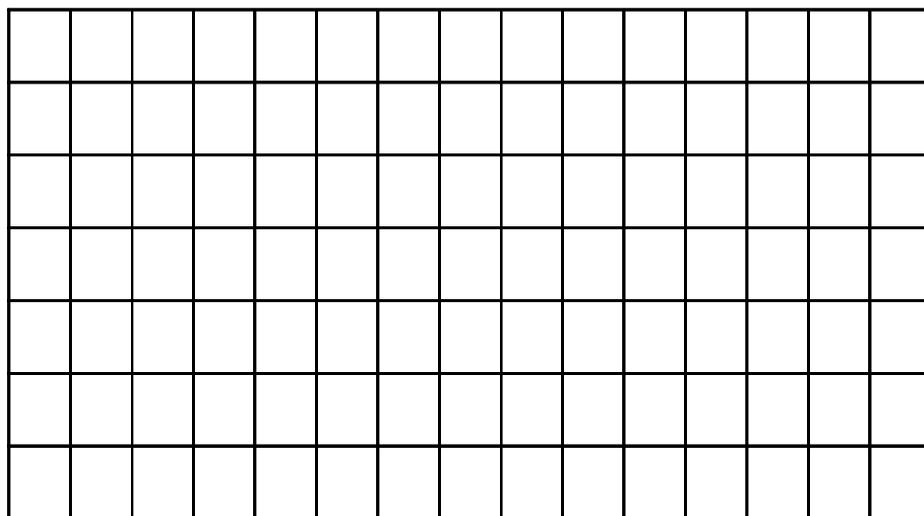
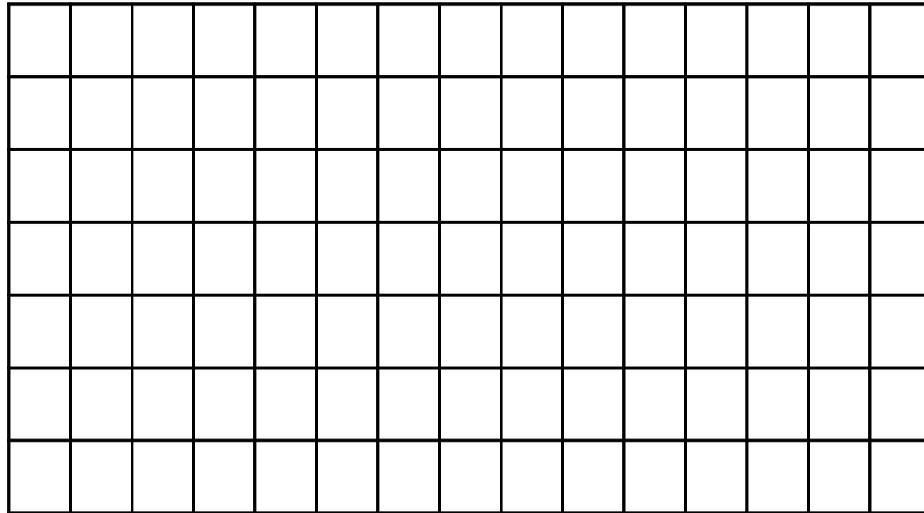
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Plotting Force Curves for Bacterial Transport Scenario, Simulation 1



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Plotting Force Curves for Bacterial Transport Scenario, Simulation 2



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Questions, Simulation 2:

7. For each value of pH, at what approximate distance does the approach curve move away from zero? Is the initial force repulsive or attractive?
8. Is the repulsive force greater at pH 5 or pH 7?
9. Based on your answers to the questions above, would you predict that the bacteria adhere (stick) to the surfaces better at pH 5 or pH 7? Does this agree with what you observed in the bacterial transport column experiments?

The scientist then calculated the “sticking efficiency” of the bacteria to the mineral surface under different values of ionic strength and pH. The higher the sticking efficiency, the stronger bacteria will adhere to the mineral. The table of values is below.

Sticking Efficiencies for *E. coli* and Silica at Different Values of pH and Ionic Strength.

pH value	Ionic Strength	Sticking Efficiency
5	0.005	3.6×10^{-8}
5	0.050	2.6×10^{-4}
6	0.005	9.6×10^{-16}
6	0.050	5.7×10^{-33}
7	0.050	0

10. Based on the sticking coefficient data, do bacteria stick to surfaces better at lower or at higher pH? Why? Does this answer agree with the AFM data?
11. Do bacteria stick to surfaces better at lower or higher ionic strength? Why? Does your answer agree with the AFM data?
12. Which affects the sticking efficiency of bacteria more: ionic strength or pH?
13. If you were the town engineer, could you prevent the contamination problem from reoccurring? If so, what would you do?

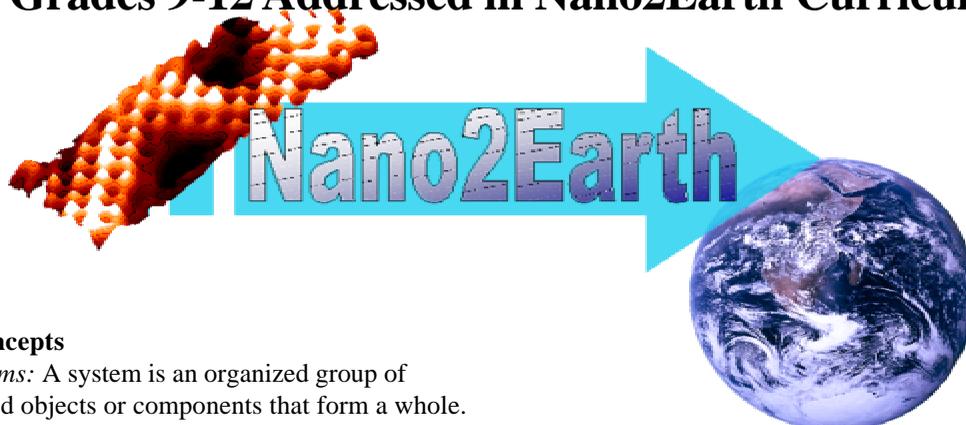
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Force Curve Data Table for Bacterial Transport Scenario

	High ionic strength	Low ionic strength	pH 5	pH 7
d (nm)	approach	approach	approach	approach
75	-0.019	-0.009	-0.019	-0.008
70	-0.023	-0.007	-0.014	0.017
65	-0.014	-0.005	-0.014	0.028
60	-0.005	-0.004	0.001	0.038
55	-0.002	-0.002	-0.002	0.060
50	-0.004	0.001	-0.004	0.086
45	-0.003	0.000	-0.003	0.112
40	-0.025	-0.003	-0.022	0.162
35	-0.024	-0.001	-0.016	0.210
30	0.012	0.001	0.012	0.271
25	-0.254	0.004	-0.254	0.269
20	-0.487	0.007	-0.487	0.080
15	-0.775	0.010	-0.876	-0.194
10	-1.004	-0.062	-1.004	-0.350
5	-1.496	-0.374	-1.436	-0.736
0	-1.701	-0.502	-1.593	-0.919

Appendix

National Science Education Standards for Content in Grades 9-12 Addressed in Nano2Earth Curriculum



Unifying Concepts

- *Systems:* A system is an organized group of related objects or components that form a whole. Thinking and analyzing in terms of systems will help students keep track of mass, energy, objects, organisms, and events referred to in the other content standards.
- *Evidence* consists of observations and data on which to base scientific explanations. Using evidence to understand interactions allows individuals to predict changes in natural and designed systems.
- *Models* are tentative schemes or structures that correspond to real objects, events, or classes of events, and that have explanatory power.
- *Explanations:* Scientific *explanations* incorporate existing scientific knowledge and new evidence from observations, experiments, or models into internally consistent, logical statements.
- *Changes* in systems can be quantified. Evidence for interactions and subsequent change and the formulation of scientific explanations are often clarified through quantitative distinctions – measurements.
- *Measurement:* Scale includes understanding that different characteristics, properties, or relationships within a system might change as its dimensions are increased or decreased.
- *Form and Function:* The form or shape of an object or system is frequently related to use, operation, or function. Function frequently relies on form. Understanding form and function applies to different levels of organization.
- *Design and Conduct Scientific Investigations:* Designing and conducting a scientific investigation requires introduction to the major concepts in the area being investigated, proper equipment, safety precautions, assistance with methodological problems, recommendations for use of technologies, clarification of ideas that guide the inquiry, and scientific knowledge obtained from sources other than the actual investigation.
- *Using Technology and Mathematics to Improve Investigations and Communications:* A variety of technologies, such as hand tools, measuring instruments, and calculators, should be an integral component of scientific investigations. The use of computers for the collection, analysis, and display of data is also a part of this standard. Mathematics plays an essential role in all aspects of inquiry. For example, measurement is used for developing explanations, and charts and graphs are used for communicating results.
- *Formulate and Revise Scientific Explanations and Models using Logic and Evidence:* Student inquiries should culminate in formulating an explanation or model. Models should be physical, conceptual, and mathematical.
- *Recognize and Analyze Alternative Explanations and Models:* This standard emphasizes the critical abilities of analyzing an argument by reviewing current scientific understanding, weighing the evidence, and examining the logic so as to decide which explanations and models are best.
- *Communicate and Defend a Scientific Argument:* Students should develop abilities associated with accurate and effective communication. These include writing and following procedures, expressing concepts, reviewing informa-

Science as Inquiry

- *Identify Questions and Concepts that Guide Scientific Explanations:* Students should formulate a testable hypotheses and demonstrate the logical connections between the scientific concepts guiding a hypothesis and the design of an experiment.

tion, summarizing data, using language appropriately, developing diagrams and charts, explaining statistical analysis, etc.

- *Understanding about Scientific Inquiry:* Scientists rely on technology to enhance the gathering and manipulation of data. New techniques and tools provide new evidence to guide inquiry and new methods to gather data, thereby contributing to the advance of science.

Physical Science

- *Structures and Properties of Matter:* The physical properties of compounds reflect the nature of the interactions among its molecules. These interactions are determined by the structure of the molecule, including the constituent atoms and the distances and angles between them.
- *Chemical Reactions:* A large number of important reactions involve the transfer of either electrons (oxidation/reduction reactions) between reaction ions, molecules, or atoms.
- *Motions and Forces:* The electric force is a universal force that exists between any two charged objects. Between any two charged particles, electric force is vastly greater than the gravitation force.

Life Science

- *The Interdependence of Organisms:* The atoms and molecules on the earth cycle among the living and nonliving components of the biosphere.
- *Matter, Energy, and Organization in Living Systems:* The complexity and organization of organisms accommodate the need for obtaining, transforming, transporting, releasing, and eliminating the matter and energy used to sustain the organism.

Earth and Space Science

- *Geochemical Cycles:* The earth is a system containing essentially a fixed amount of each stable chemical atom or element. Each element can exist in several different chemical reservoirs. Each element on earth moves among reservoirs in the solid earth, oceans, atmosphere, and organisms as part of geochemical cycles.

Science and Technology

- *Understanding about Science and Technology:* Science often advances with the introduction of new technologies. Solving technological problems often results in new scientific knowledge. New technologies often extend the current levels of scientific understanding and introduce new areas of research.

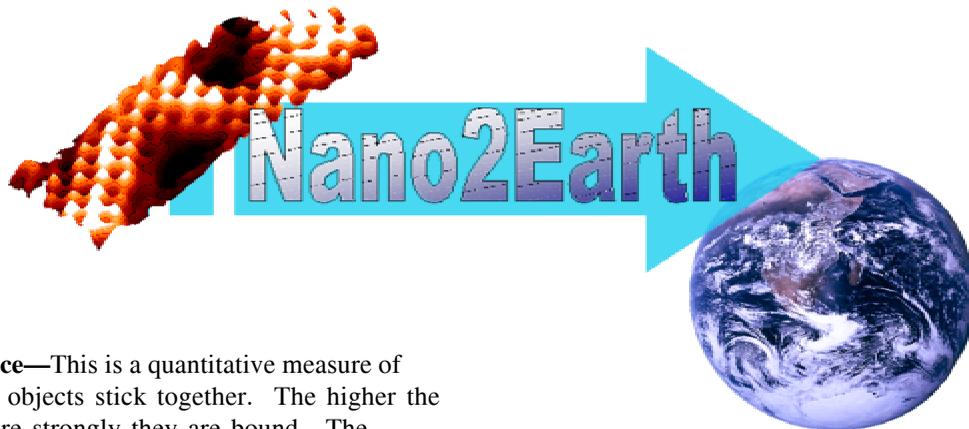
Science in Personal and Social Perspectives

- *Natural Resources:* Humans use many natural systems as resources. Natural systems have the capacity to reuse waste, but that capacity is limited. Natural systems can change to an extent that exceeds the limits of organism to adapt naturally or humans to adapt technologically.
- *Environmental Quality:* Natural ecosystems provide an array of basic processes that affect humans. Those processes include maintenance of the quality of the atmosphere, generation of soils, control of the hydrologic cycle, disposal of wastes, and recycling of nutrients. Materials from human societies affect both physical and chemical cycles of the earth.
- *Natural and Human Induced Hazards:* Natural and human-induced hazards present the need for humans to assess potential danger and risk.
- *Science and Technology in Local, National, and Global Challenges:* Individuals and society must decide on proposals involving new research and the introduction of new technologies into society.

History and Nature of Science

- *Science as a Human Endeavor:* Individuals and teams have contributed and will continue to contribute to the scientific enterprise. Science is not separate from society but rather science is part of society.
- *Nature of Scientific Knowledge:* Because all scientific ideas depend on experimental and observational confirmation, all scientific knowledge is, in principle, subject to change as new evidence becomes available.
- *Historical Perspectives:* The historical perspective of scientific explanations demonstrates how scientific knowledge changes by evolving over time, almost always building on earlier knowledge.

Glossary of Scientific and Technical Terms



Adhesion force—This is a quantitative measure of how strongly objects stick together. The higher the force, the more strongly they are bound. The adhesion force between two small objects can be measured using an *Atomic Force Microscope*. The objects are brought together (approach curve) and then pulled apart (retraction curve), a process known as a *force curve*. The adhesion force can be determined from the lowest point on the retraction (pulling apart) curve, where the force between the two objects is the greatest. By convention, this is as a negative number, so it is necessary to take the absolute value.

Adsorption—Dissolved contents of water, for example in rivers, lakes, oceans, and groundwater, are often attracted to the surfaces of minerals and bacteria with which they come into contact. The process of dissolved materials binding to surfaces is known as adsorption. In the environment, the dissolved materials typically contain ions such as the contaminants arsenic (AsO_4^- , etc.) and lead (Pb^{2+}) along with small organic materials. The amount of adsorption is related to the chemistry of the water, including its pH and ionic strength.

Aerobic and anaerobic respiration—Organisms respire to gain energy by converting high-energy compounds such as fats and sugars into the low-energy compound carbon dioxide (CO_2). The energy is obtained by transferring electrons from an electron donor (the fats and sugars) to an electron acceptor. The most energy can be obtained by using oxygen (O_2) as an electron acceptor, a process known as aerobic respiration. When other substances are used as an electron acceptor (Fe^{3+} , $\text{Mn}^{4+/3+}$, NO_3^- , SO_4^{2-} , etc.), this is known as anaerobic respiration. Typically, when oxygen is present aerobic respiration will dominate because organisms obtain more energy by using oxygen as the electron acceptor. Humans, animals, and plants can only respire with oxygen (when you exercise for a

while and your muscles are sore, that's a different phenomenon from anaerobic respiration). Some bacteria can respire either aerobically or anaerobically, while others can only respire aerobically or anaerobically.

AFM (Atomic Force Microscope)—The Atomic Force Microscope is a tool that is very widely used in nanotechnology. Developed in 1986, it can provide detailed images of surfaces in air and solution, sometimes down to a scale where nanometer-sized features can be seen. The AFM is a form of a *Scanning Probe Microscope*, where a very sharp probe (often called a tip) is rastered across the surface of interest. The tip attached to the bottom of a *cantilever*, a flexible spring such as a diving board. When the tip encounters features on the surface, the cantilever bends up or down. A laser reflecting off the back of the cantilever is typically used to record the signal, and an image is formed. Alternatively, an object can be put on or underneath the cantilever and forces between objects can be measured by collecting a *force curve*.

Angstrom—This has the value of 0.1 nm, or 10^{-10} m.

Cantilever—A cantilever is a flexible spring-like object (you can think of a diving board as an analogy). The cantilever in an *Atomic Force Microscope* flexes upward or downward depending on the attractive or repulsive forces experienced between the sample and whatever is attached to the cantilever (a tip or bacteria, for example). The cantilever obeys *Hooke's Law*, which means the amount of bending experienced by the cantilever is directly related to the force the cantilever is experiencing.

Critical zone—This zone is a place where the land meets the fluid envelopes of the Earth, the hydrosphere and

atmosphere and biological activity, weathering and fluid transport occurs.

Cryptosporidium—This is a single-celled animal. Human ingestion of *Cryptosporidium parvum* is one of the leading causes of waterborne disease in the United States.

E. coli—A common bacteria found in the human body, *E. coli* is used as an indicator of groundwater contaminated by sewage. *E. coli* is also one of the most studied bacteria in laboratory experiments.

Eutrophication—Eutrophication is the decay process in which overabundant algal growth uses oxygen which decreases the dissolved oxygen available for the other aquatic life dependent upon dissolved oxygen.

Force curve—A measurement made by an *Atomic Force Microscope*, a force curve involves bringing the tip or other object attached to the cantilever (such as a bacteria-covered bead) in contact with a sample (approach curve) and then pulling them apart (retraction curve). The force curve starts with the greatest separation, where there are no interaction forces.

Giardia—Similar to *Cryptosporidium*, *Giardia lamblia* is a single-celled parasitic animal that is responsible for causing infection when untreated water is ingested.

Heterogeneous catalyst—A catalyst is something that causes a chemical reaction to proceed that is energetically favorable, but kinetically hindered. For example, fuel combustion by automobiles creates several gaseous compounds that are potentially harmful when released to the atmosphere. In cars today, the exhaust stream passes through a catalytic converter, which is a solid material (aluminum oxide) that causes some of these compounds to convert to more stable and less harmful gases when they come in contact with its surface.

Hooke's Law—This law states that the force experienced by a spring is directly proportional to the displacement (either stretching or squishing) away from the equilibrium position.

The proportionality constant is known as the force constant k . For a one-dimensional motion of the spring, the relationship can be written as

$$\text{Force} = kx$$

where x is the displacement in the x direction.

Hydrophobic force—Water molecules are strongly attracted to each other due to the fact that they have a distribution of positive and negative charges (a permanent dipole moment; water is polar). This interaction is called hydrogen bonding. Other types of molecules and solids do not have this separation of charge distribution; they are nonpolar. Examples of nonpolar substances are oil and nonstick coatings on cooking pans. Nonpolar materials tend to be “pushed” away from water because the water molecules are more strongly attracted to each other than the nonpolar substance. This is the nature of the hydrophobic, or “water-hating” force.

Ionic strength—The dissolved constituents of a solution contribute to the properties of that solution. The ionic strength is a quantitative determination of the dissolved species, accounting for the fact that those species with higher charge change the properties of the solution more.

Iron respiration—This is a form of *anaerobic respiration*, when either Fe^{3+} is the electron acceptor or Fe^{2+} is the electron donor.

Jump to contact—This is a feature in a force curve measured by an *Atomic Force Microscope*. Regardless of whether or not the initial interaction between the tip (or bacteria, etc.) and sample is attractive or repulsive, eventually they snap into contact as they are brought together (the approach curve). This is due to forces such as van der Waals forces.

Laser—This “coherent” beam of light is all at the same wavelength. We see different

wavelengths in the visible spectrum as colors, so lasers can be red, green, etc.

Microbeads—Microbeads are beads that have dimensions of micrometers (otherwise known as microns). One micron is 10^{-6} meters, or 1000 nanometers.

Molecular nanotechnology—A term coined by the Foresight Institute, this term refers to a vision of the future. Proponents of molecular nanotechnology claim that in the future, nanoscale machines will be able to synthesize almost any material from its constituent atoms.

Nano—The value of nano is one billionth of a meter, 10^{-9} meters.

Nanobiogeochemistry—This is the interdisciplinary study of interactions between biology, chemistry, and geology that occurs over the length scale of nanometers.

Nanofilm—A nanofilm is a film which may be continuous in two dimensions but very thin (<100 nm) in the third dimension.

Nanoforce—This refers to a force on the order of a *nanoNewton*.

Nanometer—The value of a nanometer is 1×10^{-9} or a billionth of a meter.

NanoNewton—A Newton is the *System International* accepted scientific unit of force. A nanoNewton is 10^{-9} Newtons, or a billionth of a Newton. Forces between individual molecules typically fall in this range. One nanoNewton is approximately equivalent to the gravitational force between someone sitting at a computer and the computer monitor, or the gravitational force between two people at opposite ends of a moderately sized room.

Nanorange—Typically this refers to a field considered to be 1-100 nanometers.

Nanoscale—Typically this size is considered to be 1-100 nanometers.

Nanoscience—This is a field of science that measures and explains the changes of the

properties of substances as a function of size; these changes occur in the range of approximately 1-100 nanometers.

Nanotechnology—The *National Nanotechnology Initiative* of the United States defines nanotechnology as:

1. Research and technology development at the atomic, molecular or macromolecular levels, in the length scale of approximately 1-100 nanometer range.
2. Creating and using structures, devices and systems that have novel properties and functions because of their small and/or intermediate size.
3. Ability to control or manipulate on the atomic scale.

National Nanotechnology Initiative (NNI)—The National Nanotechnology Initiative is a federal program designed to coordinate research and development in nanoscale science, technology, and engineering. See www.nano.gov.

pH—Defined as the negative logarithm of the activity of hydrogen ions in solution, this number refers to the amount of free acid (H^+) or base (OH^-) in solution. Acidic solutions have pH less than 7; basic solutions have pH greater than 7.

Probeware—This is an educational technology tools designed for the science classroom. A number of different probes (light sensor, pH meter, dissolved oxygen probe, etc.) can be linked to computers for data collection and analysis.

Radionuclides—Elements may exist with various numbers of neutrons in the nucleus, called isotopes. Isotopes with extra neutrons are sometimes unstable, and spontaneously decompose with release of

various forms of radiation. These unstable isotopes are known as radionuclides.

Reduction of iron—When microbial activity is responsible, this usually refers to a form of *anaerobic respiration*, when Fe^{3+} is the electron acceptor.

Salmonella—This is a group of bacteria that commonly live in animals, but can cause gastrointestinal disease in humans.

Scaling—Materials behave differently when scaled down in size.

Scanning Probe Microscopy (SPM)—This refers to a family of microscopes that all involve the rastering of a probe (sometimes called a tip) across a surface. Examples of scanning probe microscopes include the *Atomic Force Microscope* and the original Scanning Probe Microscope, the *Scanning Tunneling Microscope*.

Scanner—This scanner is a device on the *Atomic Force Microscope* to move a sample closer and further from the tip, and/or from side to side.

STM—Scanning Tunneling Microscope—This is a microscope in which a metallic tip is rastered across the surface of a conducting or semiconducting material. An image is obtained by electrons that transfer (tunnel) in or out of the sample. The tunneling current depends exponentially on the distance between the sample and the tip, such that even atomic scale images have frequently been obtained.

Transmission Electron Micrograph—This is a picture taken by the Transmission Electron Microscope. A TEM uses a beam of electrons to image extremely small features in materials, including the internal structure and chemistry.

Although they have been around for over 70 years, continual improvement in technology has improved TEMs to the point that they are now capable of imaging individual atoms in some situations. Electrons are effective for imaging small features because they can be accelerated to the point that the electron beam has a wavelength approximately equal to atomic dimensions (Angstroms). Light microscopy is limited to features of approximately 300 nm due to the wavelength of light.

Winogradsky column—This column is designed to simulate a natural ecosystem. Mud and water collected from a lake, stream, creek, or puddle are placed into the column.

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 Page 106 Map of arsenic concentrations in Bangladesh from <http://bicn.com/acic/>, the West Bengal and Bangladesh arsenic crisis information centre.



Appendix A

Morphological and chemical-physical characterization of Fe doped synthetic chrysotile nanotubes

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Appendix B

Earth's nano-compartment for toxic metals

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ABSTRACT

Nanoscale materials, both inorganic and organic, appear to be ubiquitous in the environment. Recent investigations into the nanoscale chemistry and mineralogy of toxic metal distribution in nature have revealed novel and unexpected insights. Additionally, corresponding advances in the field of nanoscience have demonstrated that the physical properties and reactivity of nanomaterials vary dramatically as a function of the material size. Geoscientists are uncovering a fascinating story of how the immense surface area, unusual properties, and widespread distribution of natural nanomaterials often affect the fate of toxic metals in ways that are surprising.

INTRODUCTION

Metals that move through our environment, in whatever geo-compartment they are in, must traverse interfaces in order to communicate (react) with living things. That is when these metals are of the most interest to us, sometimes as a nutrient, often times as a toxin as is so apparent from this issue of *Elements*. When looking at the Earth's interfacial system, it has been estimated that there are trillions of square kilometers of interfacial area between the hydrosphere, atmosphere, and solid portions of this planet (Hochella and White 1990). In fact, if one is interested in this interface from a fundamental chemical flux or exchange point of view as we are with toxic metals, then it is convenient to think about interfacial areas not in terms of square kilometers, but square nanometers. This is the area within which fundamental surface phenomena happen. In that frame of reference, it is interesting, and perhaps overwhelming, to note that a conservative estimate of the inorganic and biological surface area in the near-surface region of the Earth amounts to something in the ballpark of 10^{34} square nanometers (Lower et al. 2002). To help put a number this large into perspective, the farthest known galaxy in the universe is “only” 10^{26} meters away.

Clearly, we are dealing with a realm of the Earth that is unimaginably large, not to mention complex. Perhaps most striking, however, is that the majority of this interfacial area is *completely* unseen to the unaided eye. This vast store of surface area belongs to very small particles. The smallest of them, the nanoparticles, possess by far the most surface area per mass of all particulate matter. As just one simple example, if a cube 1

mm on a side is divided up into cubes 1 nm on a side, the mass remains the same (naturally), but the surface area increases by a factor of a million.

Yet, as we will see in this article, the dominance in surface area attributed to very small particles is only half the story. The other half is that nanoparticles typically have dramatically different properties than larger particles of the same material. This is, in essence, the basis of the field of nanoscience.

In this article, we will briefly look at why nanoparticles have unusual properties, where they are in the environment, and how they can play a key role in the distribution and reactivity of toxic metals in those environments. We should emphasize from the outset that this subject is in a relatively early stage of development. We estimate that large gaps in our knowledge of this area exist, making it an exciting time of new realizations, discovery, and change.

WHAT MAKES NANOPARTICLES SO DIFFERENT THAN THEIR LARGER COUNTERPARTS?

Consider H_2O , the best known and arguably most remarkable molecule on Earth. In the pressure-temperature phase diagram for H_2O , there is a triple point at 273.16 K and 611.2 Pa. At this point, of course, H_2O gas, liquid, and solid (that is water vapor, water, and water ice, respectively) are in chemical equilibrium. Now, let's put a twist on this common, although still remarkable story by asking a question. If you started with a

single H₂O molecule, which would therefore be H₂O as a gaseous component, how many H₂O molecules would you need to add in close proximity before that cluster has the identical physical and chemical properties of bulk water liquid, or in an ordered arrangement, bulk water ice. Two H₂O molecules, 10, or 1,000? This is actually a very, very difficult question to answer, as it depends on the property that one wishes to measure. Nevertheless, whatever the answer, the point should now be clear: there *must* be a transitional zone between molecular and bulk-like properties. The properties encountered here are neither molecular-like nor bulk-like, and as such, they are often strange to us, and constantly changing as we go through this transitional zone. Yet if the material that we are interested in is in this size range, as it turns out materials in the nano-size range are, then we better pay attention.

Let's look at this from an electronic structure point of view, simplified to be sure (for example, we will ignore orbital hybridization), but nevertheless providing us with a highly useful framework. Imagine that you observe a single metal atom, say Mg, as well the dimer Mg₂, the trimer Mg₃, and so on to Mg_n. We can look at the electron energies of a single Mg atom and see how they change in larger and larger clusters of Mg atoms. We will concentrate on the electrons that make up the valence band (resulting in bonds between atoms) and the conduction band (resulting in metallic behavior). For Mg, the valence electrons will have 3s character (the highest filled shell for element 12), and the conduction band states will have 3p character (the lowest unfilled shell for element 12). For a single atom (that is n=1), as shown in Fig. 1, both of these levels have discrete, well defined energies. When n = 2, that is for the dimer Mg₂, the single 3s level splits into

two what we now call molecular orbitals, and both are full. The empty 3p level also splits and remains empty. As more Mg atoms are added to our cluster, more molecular orbitals are added, so that for Mg_n , there will be n molecular orbitals, all at slightly different energies. As a consequence, and as illustrated in Fig. 1, as atoms are added to our cluster, the molecular orbitals fan out. This is the well known electronic structure transition from a single atom with discrete energy states to a cluster to a bulk-like state with electronic “bands”. As n increases, the 3s and 3p bands eventually overlap, and filled states in the 3s valence band spill into the empty states of the 3p band. When this happens, the “band gap” becomes zero, and the cluster takes on bulk behavior in terms of electrical conduction. That is, at this point, the cluster is electrically metallic. Before, with a non-zero band gap, it was a semiconductor.

It recently became possible to “build” Mg atom clusters from Mg_2 on up in size, a remarkable feat, and the 3s and 3p states have been directly observed in these clusters with photoelectron spectroscopy (Thomas et al. 2002). The behavior shown in Fig. 1 is observed. As the cluster size builds, the band gap closes. At a cluster size of 18 Mg atoms, the band gap goes to zero. A semiconductor-to-metal transition occurs due to the increase in cluster size, wholly within the nanorange.

Reactivity as a function of size

As fundamental properties of a material change with size, as we have seen, one would expect that the reactivity of that particle in a chemical reaction should change as well.

An elegant example of such a case is found in the use of gold catalysts on titania substrates to oxidize CO to CO₂ (Valden et al. 1998). As shown in Fig. 2, gold islands on titania are most active at driving this oxidation reaction when they are 2 to 3 nm in diameter. At sizes larger than this, their reactivity drops off considerably. Other examples of the reactivity of materials, including metals, sulfides, and oxides, as a function of size can be found in, for example, Alivisatos (1996) and Bell (2003).

Mineral nanoparticles

Minerals in the size range of approximately a few to several tens of nanometers are in the transitional range where properties are expected to be variable and deviant from bulk behavior. Although changes in the electronic structure with particle size in the nanorange is expected, even for insulators such as most minerals (Noguera et al. 2002), there are other ways to rationalize property changes with size, typically depending on how one is observing these changes. One can take a thermodynamic approach and use surface free energy to predict nanoparticle stability (e.g. Navrotsky 2001). One can also take a structural approach, looking at the internal and surface atomic structure of nanoparticles, including changes in surface site distribution with a change in size (e.g. Waychunas 2001; Kim et al. 2004). Finally, one can consider how these changes in electronic structure and bonding may influence surface redox processes using electron transfer theory (Madden and Hochella 2005).

There is more and more direct evidence recently from X-ray absorption spectroscopy of transition metal oxides that as the particles get smaller (below 10 nm), there is a decrease in the symmetry of metal surface sites (e.g. Chen et al. 2002; Zhang et al. 2003). As hypothesized by Madden and Hochella (2005), this kind of site distortion has important implications for metal binding, as well as electron transfer in associated redox reactions. They have observed that as hematite nanoparticles get smaller, from grain diameters of 40 nm to 7 nm, they drive aqueous Mn^{2+} oxidation reactions dramatically faster, up to two orders of magnitude faster after surface area normalization.

WHERE ARE NANOPARTICLES IN THE ENVIRONMENT?

What we have discussed in this last section is of remarkable academic interest, but why should Earth scientists care if nanoparticles are not common in the hydrosphere, atmosphere, and in soils. In fact, now that we are looking more than ever, we are finding them everywhere.

In the hydrosphere, including pore water in soils, it has been convenient to consider water soluble species as whatever passes through a 0.2 μm (200 nm) filter. From what we now know about nanoparticles, this notion will clearly not always be the case. For some time, a few aqueous geochemists and soil scientists have realized the importance of the transport of species complexed in or on organic (biopolymer, humic substance, etc.) and inorganic (mineral) nanoparticles and not as dissolved entities (e.g. Buffle and van Leeuwen 1992; Grolimund et al. 1996). Although actual experimental, microscopic, and

field data are still quite sparse to further support these notions, one can reasonably estimate that it is just a matter of time before such evidence will be common, and a more complete picture of nanoparticles in water and in soils will form. This includes their movement and lifetime (the latter because some portion will be in early stages of aggregation and growth). Even now, outstanding studies are beginning to appear that clearly show the importance of nanoparticulate transport of metals in the environment (e.g. Warren and Haack 2001; Allard et al. 2004; Lowry et al. 2004). Ruben Kretzschmar's article in this issue of *Elements*, on metal retention and transport on these and larger particles in the environment, also gives a broad overview of this topic.

The flux of mineral dust entering the atmosphere, derived from wind blowing over the world's soils, has been estimated to be in the neighborhood of 10^{15} grams per year (e.g. Seinfeld and Pandis 1998). This far exceeds the annual average mineral dust from volcanic eruptions, as well as the amount of dust from biological debris. Minerals that precipitate from sea spray, a common natural aerosol, represent the only form of dust that rivals soil derived mineral dust (e.g. O'Dowd et al. 1997). The average particle size of airborne mineral dust, based on mass, is between 2 and 5 μm . However, based on number of particles, the average size is approximately 0.1 μm (100 nm) with a considerable number below this value well into the nanorange (Klein 1993; Buseck et al. 2000; Anastasio and Martin 2001). The heterogeneous chemistry that occurs between mineral dusts and atmospheric gases, as well as the direct and indirect radiative forcing (heating or cooling) caused by the particles, is little understood, but thought to be very important (Buseck et al. 2000).

To date, the best single source for a catalog of nanoparticles in the environment, as well as their characteristics and properties as best we know them at this point, can be found in a collection of papers edited by Banfield and Navrotsky (2001).

NANOPARTICLES AND TOXIC METALS IN THE REAL WORLD

Great advances have been made in the speciation of toxic metals in real world materials (soils, sediments, natural waters, etc.) as evidenced by the accompanying articles in this issue of *Elements*, as well as articles such as Manceau et al. (2002). In addition, there are now several examples in the literature where environmentally important nanophases have been observed and studied in relation to the toxic metals that they hold, and a few of them will be highlighted here. In the Clark Fork River Superfund Site, Montana, the largest superfund site in the United States, mining has contaminated over 1,600 km² of land with Pb, As, Zn, and Cu. In many areas, even Zn and Cu are over the toxic threshold of most flora and fauna. All these metals are distributed among millions of cubic meters of mine tailings that have moved down the Clark Fork River drainage over the last one and a half centuries (Fig. 3a). Until recently, it was not completely clear how the metals were tied up in these highly weathered tailings, having also over time mixed with local soils and stream sediments. Therefore, metal transport mechanisms and bioavailability were difficult to fully assess. Now, analytical Transmission Electron Microscopy (TEM) has been used to give a detailed picture of where the metals are within these complex materials (Hochella et al. 2005a; Hochella et al. 2005b). Perhaps not surprisingly, most

of the toxic metal is tied up in or on nanoparticles. One of the nanophases present, ferrihydrite (a poorly crystalline hydrous iron oxide), is well known for prolific metal uptake in contaminated sediments. But a new nanophase was also discovered, one that is apparently far more reactive than even ferrihydrite at heavy metal uptake (Fig. 3b). It is a secondary manganese oxide mineral that is probably very similar to the mineral vernadite (nominally $\text{MnO}_2 \cdot n\text{H}_2\text{O}$, a poorly crystalline sheet manganate). It is likely that the ferrihydrite surfaces catalyzed aqueous manganese oxidation that resulted in the verdnadite-like phase (Hochella et al. 2005a). The extraordinary heavy-metal sorptive capability of the vernadite-like phase makes it a promising candidate as a reactive medium in permeable barriers that are used in environmental remediation.

Utsunomiya et al. (2004) have performed a fascinating study of trace heavy metals in airborne particulates collected from the Detroit, Michigan (USA) urban area.

Presumably, many of these particles are anthropogenic in origin. Several heavy metals, including a few that are closely regulated by federal agencies in many countries due to their toxicity (e.g. As, Cr, Pb, Se), were detected in particles ranging down to a few nanometers in size (Fig. 4). As pointed out in Utsunomiya et al. (2004), the inflammatory potential of these nanoparticles in lung tissue is expected to be high. Also, the chemical toxicity of these particles may be greatly underestimated if, due to their size, they show enhanced dissolution or exchange reactivity.

Finally, Suzuki et al. (2002) have recently shown that uraninite (UO_2) produced by the reduction of aqueous U^{6+} in sediments via uranium-reducing bacteria typically forms

grains that are less than 2 nm in diameter. Not only are such small particles potentially highly mobile in groundwater and surface water systems, but their solubility is expected to be much higher than bulk uraninite solubility. Therefore, bioremediation of uranium-contaminated sediments may not be as effective as anticipated, despite the efficiency of this reduction process.

In each of the three cases presented above in this section, the size of the particles holding the toxic metal of interest is critical. The properties of these nanoparticles, in their deviation from the well-known properties of the “bulk” phase, will be important in the mobility (distribution) and reactivity (bioavailability) of the toxic metal. When combined with the sheer number of nanoparticles in the environment, the great importance of this environmental compartment is clear. In this area of research, we are convinced that many new, exciting, and sometimes disturbing discoveries await us.

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FIGURES AND CAPTIONS

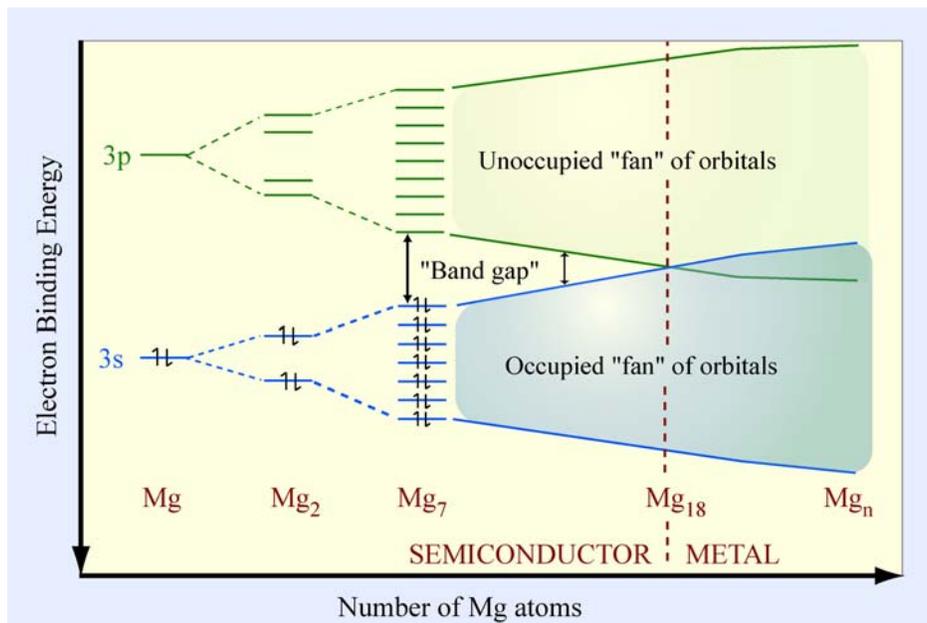


Figure 1 Energy distribution of 3s and 3p electronic states in an isolated Mg atom and larger and larger Mg clusters (adapted from Thomas et al. 2002).

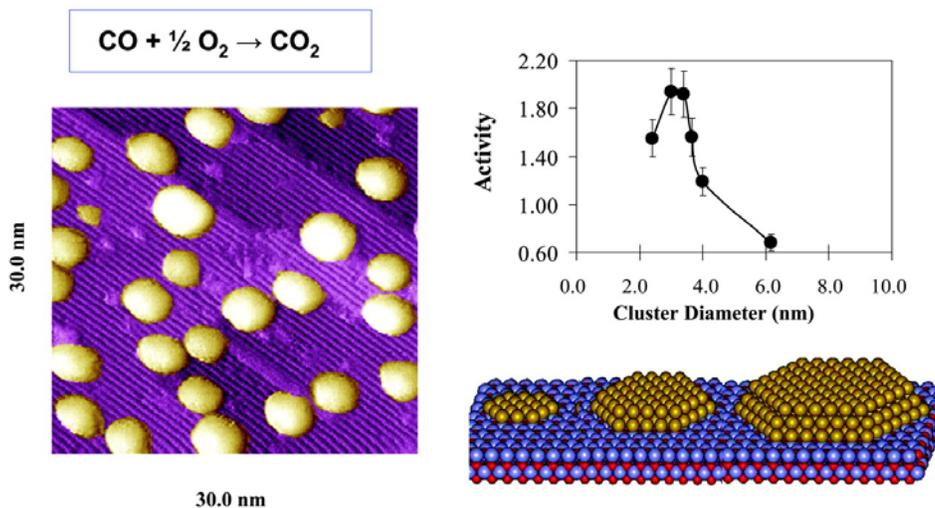


Figure 2 Gold nanoclusters deposited on titanium oxide, depending on their size, show striking variations in their ability to oxidize CO (adapted from Bell 2003).

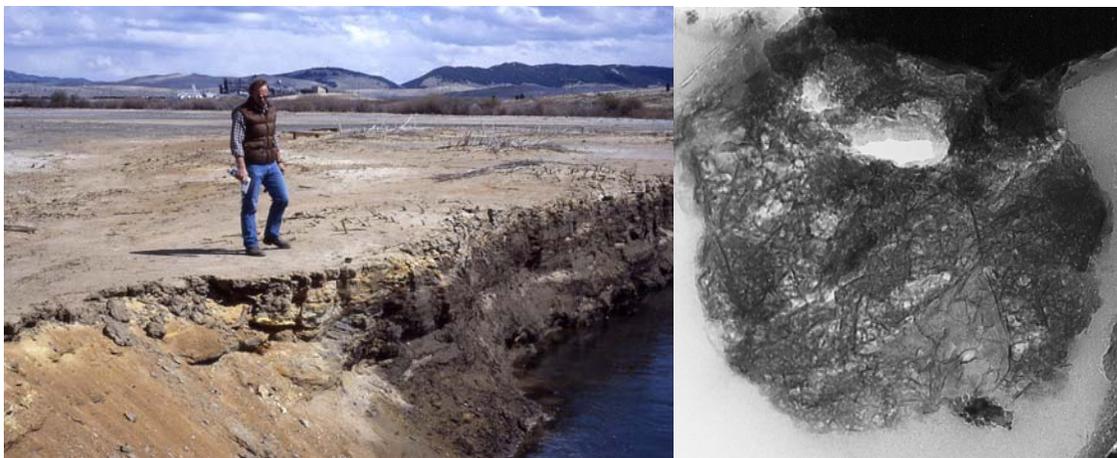


Figure 3 (a) Headwaters of the Clark Fork River, Montana (USA). Mine tailings completely cover the original floodplain surface and the high metal concentrations limit the growth of vegetation (photo courtesy of J. Moore). (b) TEM image of ferrihydrite and vernadite-like nanoparticles from weathered floodplain tailings and stream sediment. The arrows point to “strings” which consist of vernadite-like nanoparticles ranging down to 1.5 nm in diameter.

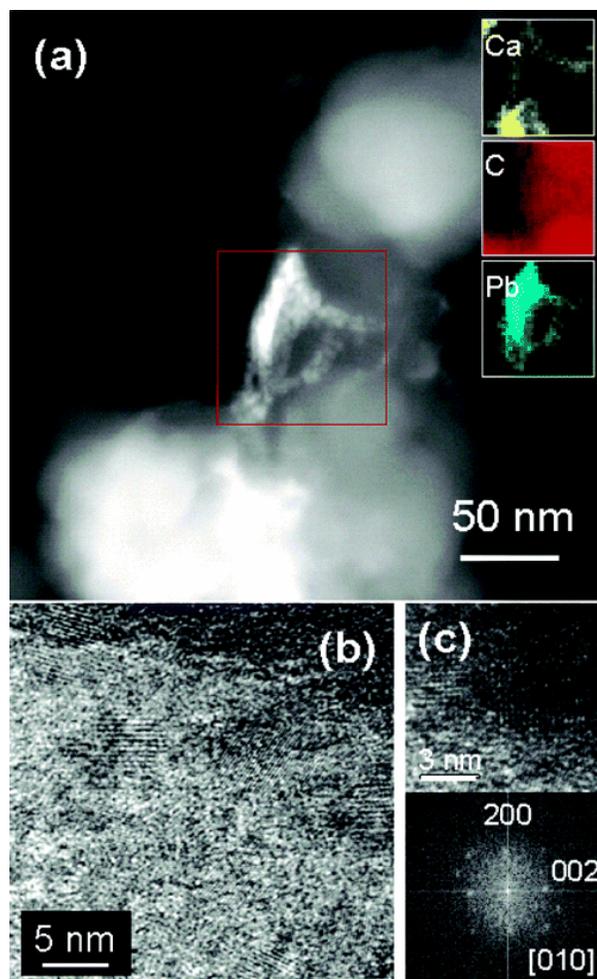


Figure 4 (a) TEM image and elemental maps of a Pb-bearing nanoparticle from urban aerosols. The nanoparticle is associated with the surface of unidentified carbonaceous matter. (b) High Resolution (HR)TEM image of the Pb-bearing nanoparticle showing that it is an aggregation of particles that range down in size to a few nanometers. (c) HRTEM and Fast Fourier Transferred image used to identify the nanoparticles as PbO (from Utsunomiya et al. 2004).