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Nanogeoscience: From the Movement of Electrons to Lithosphere Plates

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Researchers of nano-scale science explore the workings of nature in the dimensional space spanning a single nanometer (nm) to about 100 nm. While geoscientists pride themselves on looking at very large-scale, highly complex processes, the origins of nearly all things geologic are rooted deeply in nanoscale phenomena. The near surface of the Earth is composed of what has been conservatively estimated as 10³⁰ square nm of inorganic and biological surfaces [Hochella and White, 1990; Whitman et al., 1998]. These two types of surfaces have been interacting for over 3 billion years on our planet. A growing number of geoscientists, supported by U.S. agencies such as the National Science Foundation (NSF), the Departments of Energy and Defense, and even the National Institutes of Health, are embracing the intricate nano-scale world and helping to forge the frontiers of nanoscience through geological studies.

Historical Perspective—Tracing the Roots of Nano-scale Science

The roots of nanoscience can be traced back to the origins of crystallography, geochemistry, and clay mineralogy. In 1913, W.H. Bragg and W.L. Bragg used X rays to make the first structure determinations of crystals, many of which were minerals. While most of their studies were at the Ångstrom level, they were perhaps the first to observe a single nanometer when they measured the *c* dimension of the unit cell of naphthalene at 0.9 nm [Bragg, 1924].A great deal of similar work allowed V.M. Goldschmidt, the father of modern geochemistry, to establish the first table of ionic radii in 1926. Also in the 1920s, researchers were finally able to establish that micrometer to submicrometer components of soils were indeed distinct crystalline minerals, and clay mineralogy was born. Clearly these geoscientists, and those who followed in their footsteps, helped to lay the foundations for what is now called nano-scale science.

Nanoscience itself was not born, even in principle, until much later. Nobel Laureate Richard Feynman was one of the first to formulate the idea that bulk material properties do not simply scale into the nanodomain. His speech titled "There's Plenty of Room at the Bottom," which he delivered at the 1959 meeting of the American Physical Society (available at http://www.zyvex.com/nanotech/feynman. html), is cited by many historians as the beginning of nano-scale science and technology. Feynman was fascinated by the possibility of manipulating single atoms to create materials and store information. For example, he estimated that by representing each letter of the alphabet with 6-7 "bits" of information-where a bit is a

dot or dash created by 100 atoms—all of the information that mankind has accumulated in all the books of the world could be written in a cube of material 200 μ m on a side. According to Feynman, the nanoscale offers "new kinds of forces and new kinds of possibilities, new kinds of effects."

An example of this can be exhibited by looking at the structure of graphite, which was determined long ago by X-ray analysis. Graphite consists of parallel sheets of hexagonal (sixmember) carbon rings. Carbon-carbon bonds within these parallel sheets are significantly stronger than those between adjacent sheets. Hence, graphite has perfect basal cleavage. If one were to take a single sheet of graphite a few nanometers across and roll it into a cylinder, one would create what we now call nanotubes. While nano-tubes and graphite are similar in structure, they possess very different properties, because one exists in the nanoscale and one does not. Consider, for example, the modulus of elasticity-Young's moduluswhich is a fundamental material constant relating stress and strain. This value for



Fig. 1. In this scanning tunneling microscope image of a pyrite (FeS₂) surface exposed to oxygen, bright spots correspond to surface iron sites (the shared sulfur dimers between adjacent iron positions are not visible). Oxidation by adsorbed oxygen alters the electronic states at iron sites, resulting in dark patches. The x and y axes are in nanometers and the z-axis reflects the tunneling current of surface electrons. Original color image appears at the back of this volume.



Fig. 2. Attractive (negative values) and repulsive (positive values) forces of interaction are shown as a function of the distance between a cell of Shewanella and goethite (FeOOH; open squares) or diaspore (AlOOH; solid circles). The upper data set for each mineral corresponds to intermolecular force measured upon approach of the mineral toward the cell. The lower data set for each mineral describes adhesion and nano-mechanical stretching of surface biopolymers as the mineral is retracted from the cell. The discrete saw-tooth pattern between 400 nm and 500 nm corresponds to an outer membrane protein produced by the bacterium to interact specifically with the goethite surface.

graphite is a few GPa (10° Pascals), while the stiffness of a nano-tube is measured in TPa (10° Pascals) [Krishnan et al., 1998]. This underscores what is considered one of the hallmarks of nanoscience. That is, as the size of a material approaches a dimension or length scale associated with a particular property for example, physical, electrical, mechanical, magnetic, thermal, or kinetic—property may change, sometimes dramatically. Oftentimes, so-called emergent properties become apparent when a material's size reaches the nanoscale.

Nanophenomena Probed Atom by Atom

Many fundamental mechanisms of reactions occur below the dimension of 1 nm at the level of atoms. Direct observation of such phenomena has been difficult. However, new tools are making it possible to directly observe elementary reactions. For example, a reaction at the site of one atom on a mineral surface can have profound effects that alter the electronic structure and reactivity of neighboring sites several nanometers away.

In one example, quantum mechanical calculations and scanning tunneling microscopy/ spectroscopy have been used to investigate the way in which oxygen and water combine to oxidize pyrite (FeS₂) [*Becker et al.*, 2001]; this process leads to acid mine drainage. Initially, molecular oxygen adsorbs to iron on the surface of pyrite to form discrete patches of oxidation bound by rows of iron atoms along the diagonal of the surface cell [*Becker et al.*, 2001] (Figure 1). These oxidized patches do not have sharp edges, but they do have a gradation in brightness that suggests a link between the oxidation of one iron site and the electronic structure of neighboring sites within proximity of 1 nm. This is because the oxygen molecule, adsorbed to a single iron atom, pulls electrons from the underlying and surrounding iron and sulfur atoms. The result is that surface sulfur atoms take on a slightly more positive charge. This, in turn, allows water molecules to mount a very effective nucleophilic attack that oxidizes the sulfur [*Becker et al.*, 2001]. Based on observations like these, new models are being developed at the nanoscale to describe the fundamental mechanism of mineral oxidation and sorption reactions at mineral surfaces.

Biomolecule Interactions with Mineral Surfaces in Force and Distance Nanospace

Interactions between biomolecules and mineral surfaces have been implicated in the origins of life (e.g., mineral surfaces may have served as templates for the synthesis of nucleic acids and proteins) and in determining the distribution and transport of micro-organisms in nature. As with the study discussed above, new techniques are allowing the discovery of previously unknown phenomena. A tool called force microscopy enables one to measure the seemingly infinitesimal forces that govern the interactions between a mineral surface and nano-scale biomolecules on a living bacterium.

Force microscopy has been used to study adhesion and electron transfer reactions between the metal-reducing bacterium *Shewanella* and oxyhydroxides [*Lower et al.*, 2001]. As the bacterium is brought to within



Fig. 3. This transmission electron microscope image shows iron oxyhydroxide and metal oxide nanoparticles from an acid-mine drainage site. Toxic metals can sorb to these nanocrystals, or toxic metal oxides can form directly in the nanometer size range. Scale bar = 200 nm.

100 nm of the mineral surface, it begins to feel attractive or repulsive forces measured in nanoNewtons (see upper two curves in Figure 2). The sign and magnitude of these nano-scale forces ultimately control whether the cell adheres to the mineral surface. Adhesive bonds are created once the cell makes contacts with the mineral, manifesting itself as a relatively strong negative force upon retraction of the cell from the mineral (see two lower curves in Figure 2). During retraction, proteins or other macro-molecules on the cell surface may be unraveled such that they provide a distinct signature in the force curve (Figure 2). By studying the expression of these proteins under different conditions, Lower et al. [2001] were able to provide quantitative evidence that bacteria actively recognize minerals such that they localize or produce biomolecules at the mineral interface.

Besides improving our understanding of bacterial adhesion to material surfaces, the ability to directly probe cell-mineral interactions at the nanoscale may lead to advances in nanotechnology. For example, one may now be able to systematically tailor the exquisite, natural specificity between biomolecules, as produced by living microorganisms, and material surfaces to fabricate intricate, nanoscale patterns of various chemical or structural features.

Environmental Interactions between Heavy Metals and Nanoparticles

A fundamental question at contaminated sites is whether heavy metals are being transported as aqueous complexes or as part of a precipitate. In the past, "dissolved" metals have been operationally defined as passing a submicron filter (typically in the 0.2 to 0.5 micron range; that is, 200 to 500 nm). However, detailed meas-

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Fig. 4. Left: This scanning electron microscope image shows aggregates of sphalerite (ZnS) associated with the long, fibrous sheaths of sulfate-reducing bacteria. Each sphere-like aggregate is composed of billions of nanometer-sized particles. Scale bar = 2μ m. At right is a high-resolution transmission electron microscope image of a nanoparticle from the aggregates shown on the left. Scale bar = 1.5 nm.

urements are now revealing that much of the "dissolved" metal is present as clusters or nanoparticles. Methodologies like electron microscopy are being brought to bear on this problem.

At one mining site characterized by acid mine drainage, Hochella et al. [1999] determined that nanoparticles, like iron oxyhydroxides and hydroxysulfates (Figure 3), can precipitate from solution and bind high concentrations of copper, lead, zinc, cadmium, and arsenic. At another mining locality it was determined that hydrogen sulfide, produced from sulfate-reducing bacteria, combines with aqueous zinc to form monomineralic, nano-crystalline sphalerite (ZnS) [Labrenz et al., 2000] (Figure 4). Many of these nano-particle aggregates, which also contain arsenic and selenium, adhere to biofilms, thereby concentrating toxic metals up to a million times relative to bulk solution levels [Labrenz et al., 2000]. Ongoing studies are examining the differences in the thermodynamic and kinetic properties of nano-crystals, as opposed to larger particles of the same chemical composition.

Nucleation and Growth of Nanoparticles

It is becoming clear that nanoparticles are found in many environments and that they control many geologically relevant processes. To fully understand the structure and reactivity of such particles, we must first understand how they form. In the classical sense, growth is thought to occur through atom-by-atom addition to an inorganic or organic template. However, the growth of nanoparticles may adhere to a very different set of rules.

It has been shown, for example, that nanoparticles of iron oxyhydroxides can selfassemble by aggregating and rotating so their structures adopt parallel orientations in three dimensions [*Banfield et al.*, 2000]. In this study, *Gallionella* and *Leptothrix* bacteria enzymatically oxidized ferrous iron in the water column. This led to a supersaturated solution and caused the precipitation of 2–3 nm particles of ferrihydrite (nominally 5Fe₂O₃ (9H₂O), which aggregated or attached to negative moieties on the outer surface of the microbial cells. Brownian motion and other forces caused these nanoparticles to rotate, water was eliminated at coherent or semi-coherent particleparticle interfaces, and iron-oxygen bonds formed between adjacent nanoparticles and converted them into larger single crystals [Banfield et al., 2000]. Growth by oriented attachment has important implications for material reactivity because adsorbed ions may become incorporated into a growth aggregate as point defects. This could decrease the bioavailability of these ions, as well as modify the thermodynamic and kinetic properties of the phase material.

The Future of Nano-scale Science and Technology

The U.S. National Science Foundation (NSF) is sponsoring a symposium, "Small wonders: Exploring the vast potential of nanoscience," in Washington, D.C. on 19 March 2002, to bring together scientists—including Nobel laureates—and politicians for discussions (see http://www.nano.gov/agenda.htm).

In addition, a new volume of Reviews in Mineralogy and Geochemistry titled *Nanoparticles in the Environment* (Minerological Society of America, 2001; ISBN 1529-6466), and an associated short course taught at the University of California, Davis, in December 2001, showcase a range of studies aimed at understanding recent discoveries relevant to nano-particle behavior and reactivity in our environment.

Also, a workshop supported by NSF, Lawrence Berkeley National Laboratory (LBNL), and the U.S. National Research Council is scheduled for 14–15 June at LBNL; it will bring together a broad cross-section of the geoscience community to develop ideas for future nanogeoscience research programs. For more information, contact A. Navrotsky, University of California at Davis (anavrotsky@ ucdavis.edu), or G.Waychunas, LBNL (gawaychunas@lbl.gov).

This is only the beginning. The reach of nano-scale science and technology is proving

to be anything but small. Clays are being combined with polymers to fabricate nano-composites with structural, temperature, and barrier properties superior to those of many plastics [*Manias et al.*, 2001]. These clay nanomaterials have found a use in the multi-billion dollar packaging industry and as engineering resins for automotive and industrial products.

In yet another example of the reach of nanoscience, a new theory describing friction from a nano-scale perspective may explain the fundamental mechanisms of earthquakes [Gerde and Marder, 2001]. This work shows that objects are able to slide past one another by sending nanometer-sized pulses of selfhealing cracks along the interface. This may help to explain the geophysical paradoxes about heat generated by earthquakes. Experimental tests to validate this model are still required. Nevertheless, it is simply remarkable to ponder movements on the order of single nanometers causing kilometer-scale movement of the Earth's massive lithospheric plates. To quote Alfred Wegener from his book The Origins of Continents and Oceans,"earth sciences must contribute towards unveiling the state of our planet...Further, we have to be prepared always for the possibility that each new discovery, no matter what science furnishes it, may modify the conclusions we draw."

Perhaps it is time for Earth scientists to once again develop a unifying theory to describe the Earth, but this time from a "nano-perspective."

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New Concerns Raised about Thinning Glaciers

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Several large glaciers in the West Antarctic are thinning at a dramatic rate and one of them could disappear in as little as 150 years if the current trend continues, according to new findings announced at a briefing at the AGU Fall Meeting in December in San Francisco. California

Using satellite radar altimetry and satellite radar interferometry, Andrew Shepherd, a research fellow at the Centre for Polar Observation and Modeling at University College London, studied the Pine Island, Thwaites, and Smith glaciers, which are the principal ice drainage channels for the Amundsen Sea sector of the West Antarctic Ice Sheet.

"These glaciers are thinning rapidly in terms of existing time scales," Shepherd reported.

According to Shepherd, between 1991 and 2001, the Pine Island, Thwaites, and Smith glaciers thinned by more than 15, 25, and 45 meters, respectively, where they leave the continent and begin to float. In addition, the glaciers lost more than 40, 40, and 70 cubic kilometers of ice, respectively, to the ocean. Shepherd said that ice loss raised global sea level by .4 millimeters. If the current rate of thinning continues, he estimates that these three glaciers will disappear in 550, 1,500, and 150 years, respectively. He said that glaciers typically might disappear on 10,000-year time scales.

However, he cautioned that the warming of the surface by $1-2^{\circ}$ Celsius over the past century may not fully explain the ice loss.

Some Glaciers out of Equilibrium

Research by Eric Rignot, a research scientist with the Radar Science and Engineering Section of NASA's Jet Propulsion Laboratory, also found that the Pine Island and Thwaites glaciers, as well as the Dotson glacier in the same general region, are out of equilibrium and are thinning. Rignot said his interoferometric observations found that most glaciers draining the East and West Antarctic are near equilibrium, a conclusion that differs from some earlier studies that indicated a large positive mass balance among Antarctic glaciers.

The three thinning glaciers he studied are "changing with time in a surprising manner," he said, adding that once the ice reaches the ocean, it melts from the bottom.

"My study shows that a number of areas previously believed to be gaining mass in the Antarctic are in fact close to being balanced or even losing mass," he said. "The only area which stands out as clearly out of balance is the Amundsen Sea sector of Antarctica [that is] drained by the Pine Island and Thwaites glaciers."

Rignot said that although some computer models several decades ago suggested that these glaciers in the West Antarctic could potentially collapse, there was no solid data to support the hypothesis. "We haven't been able to study this region until we had satellites up there," said Rignot. "We need a longer period of study to make sure the changes are not just hiccups."

Climate Change Manifests in Different Modes

At the briefing on issues concerning the cryosphere, another researcher presented data indicating that climate change can manifest itself in ways other than warming. Walter Tucker, research geophysicist with the Army Cold Regions Research and Engineering Laboratory in Hanover, New Hampshire, said that changing atmospheric and ice circulation patterns in the Arctic have led to rapid thinning of sea ice cover there.

"We attribute at least some of the thinning to changes in Arctic atmosphere and ice circulation patterns. While no similar trend was evident in ice thickness near the North Pole, the data unquestionably indicate a decrease in Nanoscale interactions between *Shewanella* and α -FeOOH, *Science*, 292, 1360–1363, 2001.

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total ice volume in the western Arctic Ocean," said Tucker.

Tucker noted that the analysis of recently declassified U.S. Navy submarine ice data profiles indicate a thinning of 1.5 meters in mean draft in a narrow band in the western Arctic Ocean from Alaska to 89° N between the mid-1980s and early 1990s. However, there was no evidence of a similar trend in ice drafts near the North Pole. Tucker said the difference appeared to be a major shift in the strength of the Beaufort Gyre ice circulation system, situated between Alaska, Canada, and the North Pole.

View from NSIDC

Studying the often-remote cryosphere is proving important for understanding its relationship with global climate and sea level, said Richard Armstrong, senior researcher with the U.S. National Snow and Ice Data Center (NSIDC), headquartered at the University of Colorado at Boulder.

Global mean temperatures have risen by about .6° Celsius over the past 100 years, with more than half of the increase occurring in the last 25 years, according to Armstrong. "As slight as that may seem, it's enough to make a difference. Now, long-term monitoring of a series of cold region, or cryospheric, parameters shows that for several decades the amounts of snow and ice around the world have been decreasing."

Armstrong said the extent of Northern Hemisphere sea ice is decreasing by 2–3% per decade, with the greatest reduction in extent during spring and summer, but he noted that the trends are not uniform. He said decreased amounts of snow and ice could result in a number of consequences affecting sea level, albedo feedback, stream flows, navigation, water supply, and hydropower. For further information, visit the Web site: http://www.nsidc.org.

Randy Showstack, Staff Writer

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Fig. 4. Graphs depict (a) dissolved total Hg versus DOC and (b) particulate total Hg versus POC, for all 10 stream sites as well as 7 seeps during snowmelt. (p is the probability of false correlation.) Samples for which Hg was not detected were plotted at one-half of detection limit.

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Fig. 1. In this scanning tunneling microscope image of a pyrite (FeS₂) surface exposed to oxygen, bright spots correspond to surface iron sites (the shared sulfur dimers between adjacent iron positions are not visible). Oxidation by adsorbed oxygen alters the electronic states at iron sites, resulting in dark patches. The x and y axes are in nanometers and the z-axis reflects the tunneling current of surface electrons.