REPORT OF THE

NANOGEOSCIENCE WORKSHOP

BERKELEY CA, JUNE 14-16, 2002

SPONSORED BY NATIONAL SCIENCE FOUNDATION

Executive Summary

Nanoscale phenomena are unique and important to geoscience. Recent work shows that many outcomes and rates of geochemical processes are governed by phenomena at the nanometer scale, often in small particles. Surface forces exert a disproportionate influence on the structure, chemistry, and movement of these nanomaterials in the Earth. In many cases, traditional distinctions between solutes, colloids and solids become vague.

Nanogeoscience is broadly defined to include the study of materials and processes at the nanoscale in their role in geologic processes on the Earth and other planets. Because many nanoscale phenomena are concentrated near the Earth's surface, in the region sometimes referred to as the *critical zone* and comprising land, water, air, and the immediate subsurface environment, these phenomena are of crucial importance to humans. Because processes are intrinsically molecular at the nanoscale, there is an immediate synergy and a diffuse boundary between nanogeoscience and the fields of chemistry, physics, and materials science. Furthermore, geoscientists increasingly recognize the major role played by microorganisms in geologic phenomena. There is an equally fuzzy boundary between nanogeoscience and the life sciences in this realm because microbial processes often proceed by manipulating surface forces at the nanoscale.

Nanogeoscience addresses a number of issues crucial to the geological sciences: the transport of metals and organics in the near-surface environment; global geochemical and climate cycles (including the carbon cycle); ore genesis and exploitation, soil science; microbial geochemical action; origin of life; space weathering and planetary surfaces; atmospheric particle transport and ice nucleation; and even deep Earth processes. Nanogeoscience also addresses national needs: environmental safety, national security, and human health; mining, minerals, oil, and gas; environmentally friendly manufacturing and new geomimetic materials; and agriculture and food.

Geoscientists have unique skills in aqueous and solid state chemistry, particularly in complex multicomponent systems. They study phenomena occurring on a vast range of scales, both in space (nanometers to thousands of kilometers) and time (nanoseconds to billions of years). Such a multiscale approach to scientific problems is necessary in monitoring and minimizing the effects of pollution, evaluating the toxicity of materials, and ensuring the safety of water and food supplies. Furthermore, we are just beginning to explore technological applications of the incredibly diverse and functional materials produced by geochemical and biogeochemical processes. In addition, research on

processes at the nanoscale accelerates the healthy evolution within Geosciences toward understanding geologic process from the molecular to the global scale. This evolution is important both intellectually and because the nation increasingly needs expert opinions on short-term problems, such as strategies to minimize pollution, the toxicity of materials, the safety of water and food supplies, and the identification of new useful materials for industry.

To integrate more fully into the national nanoscience initiative, the growing nanogeoscience community needs access to specialized techniques and samples and better coordination of scientific and educational activities. We need improved access to major facilities such as synchrotrons and neutron sources with EXAFS, XANES, and related x-ray spectroscopies, including those suitable for light elements, spatially resolved chemical analytical techniques, diffraction and small angle scattering, and synchrotron-based infrared spectroscopy. We also need user-friendly access to smaller, but still quite specialized, facilities which offer both equipment and expertise in electron microscopy, NMR, thermal analysis and calorimetry, x-ray diffraction, isotopic measurements, uv-visible, infrared, and Raman spectroscopy, Mössbauer spectroscopy, AFM, STM, and other probe microscopies, and other techniques. Even when a technique is relatively well established, its application to nanomaterials offers special challenges. We need to identify, synthesize, and disseminate reference nanoparticles and porous materials appropriate to the geosciences. We need new techniques for manipulating small samples, for isolating nanoclusters from solution, and for characterizing nanoparticles and nanopores. We need to complement lab studies with large-scale experiments and field trials. We need improved computational methods for molecular modeling and to better integrate theory and experiment.

We need to coordinate graduate education and offer interdisciplinary training in both concepts and techniques. Such experience often transcends the boundaries of any given discipline or institution. We need to attract and prepare graduate students for multifaceted careers in academe, industry, and government. The national laboratories have a great need for American graduates trained in nanogeoscience. We need to communicate our science to the general public and to provide guidance in policy issues in which nanoparticles are important.

A distributed center in nanogeoscience is an excellent way to serve community needs in science, facilities, education, and outreach. Enhanced funding of individual and small group research projects will complement such a center.

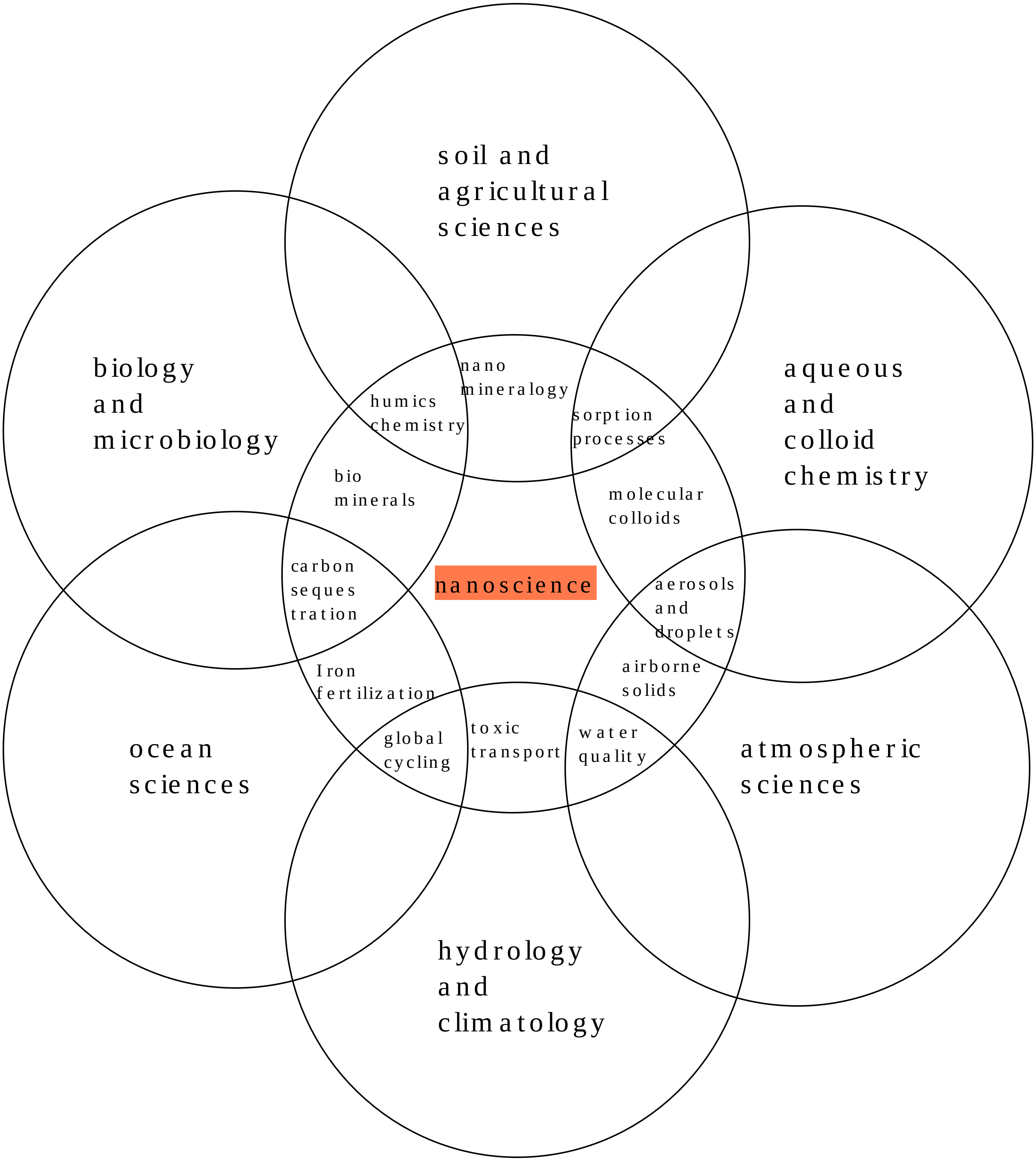
1. Introduction

Much of the chemistry in the shallow Earth occurs at disequilibrium and minerals form and dissolve in immense solubility gradients. These gradients are caused by bacterial metabolism, by the transition from oxygen-rich to anoxic environments in sediments, by the large temperature and pressure changes found in hydrothermal environments and in settings where pollution causes sharp changes in pH and metal concentrations. Recent work has shown that the initial precipitates that form in these settings can be only a few tens of atoms; they are thermodynamically metastable and some may exist for thousands to millions of years. These very fine-grained materials, or *nanoparticles*, are not only very small but they are also very common. Though they may represent only a small fraction of the *mass* of material in the Earth, they represent a large *number* fraction of the particles in atmospheric and aqueous environments, and nanoparticles are responsible for most of the *surface area* (at solid-water, solid-air, and solid-solid interfaces) of Earth materials. Because chemical reactivity is much greater at surfaces and interfaces than in the bulk, most of the chemical reactions in both natural and laboratory systems disproportionately involve nanoparticles.

Their large surface-to-volume ratio ensures that surface forces exert considerable influence over the chemistry and structure of nanoparticles and nanomaterials in general, to the point that they exhibit properties that are distinct from those of the macroscopic solid. For particles in the size range of roughly 0.5 to 500 nm, distinctions among solutes, molecular clusters, macromolecules, and colloids are vague. Also vague is the distinction between amorphous, disordered, and crystalline solids. The case for geoscientists to embrace the chemistry of nanoparticles is compelling and should be a major thrust of new research this decade.

We define ***nanogeoscience*** broadly to include the study of materials and processes at the nanoscale in their role in geologic processes on our, and other, planets. Because many nanoscale phenomena are concentrated near the Earth's surface, in the *critical zone* comprising land, water, air, and the immediate subsurface environment, these phenomena are of crucial importance to humans. Because processes are intrinsically chemical and molecular at the nanoscale, there is an immediate synergy and a diffuse boundary between nanogeoscience and the fields of chemistry, physics, and materials science. Furthermore, geoscientists increasingly recognize the major role played by microorganisms in geologic phenomena. There is an equally fuzzy boundary between nanogeoscience and the life sciences in this realm because microbial processes often proceed by manipulating surface interactions at the nanoscale.

The Venn diagram below shows how nanoscience is central to many important problems in Earth science and how nanogeoscience links Earth science to other disciplines.



Venn diagram showing overlaps of traditional environmental sciences with nanoscience. We suggest that all of such overlaps define nanoGeoscience.

This workshop of about 100 people was held at the Lawrence Berkeley Laboratory June 14-16, 2002. Its goals were: (1) to identify major scientific opportunities in the emerging field of nanogeoscience and their relation to national needs, (2) to begin to identify and organize the community in this growing field, and (3) to identify major needs of this community and begin to develop a plan, with the help of the funding agencies, for programmatic support for both universities and national laboratories in this unique and challenging area of nanoscience.

Thirty invited talks described science ranging from the energetics and kinetics of nanoparticle formation to magnetic nanocrystals synthesized by bacteria to naturally forming sulfide nanocrystals to theoretical approaches to the structure and transport of nanoparticles in air, water, and porous media. The talks were followed by breakout sessions and a small committee drafted the report.

The NSF, DOE, NASA, NRC, EPA, and ACS-PRF sent representatives who participated actively in discussion. Co-conveners were Glenn Waychunas of LBNL and Alexandra Navrotsky of UC Davis. The workshop received support from NSF, NRC, and LBNL-ESD. Appendices list the participants and the schedule and invited talks.

2. The Significance of Nanoscience to the Geoscience

The influence of nanoparticles on the Earth is potentially profound. Geoscientists have an enormous set of questions about this nanochemistry. For example, there is strong structural and chemical connection between metal-oxide and metal-sulfide nanoclusters and the active metal clusters in enzymes. Did these nanochemistries play a role in the abiotic synthesis of biomolecules leading to Archean life? How do nanoparticles interact with present day microorganisms? In particular, the growing field of geomicrobiology includes study of the production and consumption of oxides and sulfides by bacteria. Do present day natural nanoparticles have catalytic properties that influence organic matter degradation, gas hydrate formation, or other geologic processes? How do nanoparticles move in porous media? Nanoparticles also have unusual photochemical properties and quantum confinement, change in band structure, and a blue shift in light emission are well documented for semiconductors like zinc sulfide and cadmium telluride. Do natural sulfide and oxide nanoparticles show similar behavior? Can catalysis by nanoparticles generate free radicals that affect organic matter in soil, in lungs, and in the atmosphere? Do these photochemical reactions influence the cycling of organic matter or the toxicity of substances? Do sulfide minerals in the 1-10 nm size range play a role in ore deposition? Are the aggregates of nanometric particles in the ocean significant to global carbon cycling and can they modulate the cycling of key trace elements? Atmospheric particles in the range of less than a nanometer to hundreds of nanometers are ubiquitous and influence nearly all atmospheric processes. Do these nanoparticles also control the fertility of the ocean by affecting the budget of nutrients like iron?

The importance of nanoparticles extends beyond our planet. Nanoparticles are an integral component of space weathering and are so abundant on Mars that they may dominate the surface geochemistry there. Nanoparticles are present in the lunar regolith. Does interstellar dust consist of nanoparticles? Did the first condensation of solids from the planetary nebula produce nanoparticles rather than well-crystallized macroscopic crystals? Earth scientists are familiar with colloid aggregation and clay flocculation, but how do we express rate laws for the aggregation of nanoparticles that form directed chemical bonds to one another? Can we use the resulting fractal morphologies to infer geochemical conditions?

3. “Nuggets” of Recent Research in Nanogeoscience

This section contains several examples, based on one graphic and a descriptive figure caption. Its purpose is to highlight a few exciting recent developments in nanogeoscience and to demonstrate the breadth and variety of the work done.

3.1 Mineral surface adsorbates: quartz with iron

We are just beginning to appreciate the complexity of precipitate development on mineral surfaces in response to adsorbate aggregation, drying reactions, surface catalyzed reactions, and redox variations. The AFM image (top left) shows a highly polished (0.2 nm rms roughness) m-plane surface of synthetic quartz that has been exposed to a 10^{-4} M solution of Fe^{3+} at low pH. Precipitates of Fe hydroxide have formed on the surface, with a significant concentration along the edges of the step structure. The surface topology is that of steps and terraces which look like a corduroy pattern. The individual steps are 0.25 nm high, while the terraces average 80 nm in width. The cartoon crystal structure image shows what this looks like on edge. Clearly, the edge of the steps provide a unique location for initial attachment of sorbed Fe^{3+}, and later formation of oxyhydroxide precipitates. The precipitates can be analyzed in detail via grazing-incidence x-ray absorption spectroscopy (GI-XAS) done at SSRL (Waychunas 2002). This allows very thin layers of samples to be probed via EXAFS spectroscopy with unprecedented sensitivity (to less than 1% of a monolayer coverage). The graph on the lower left shows EXAFS Fourier transforms of precipitates on r- and m-plane quartz surfaces. By using the polarization of the synchrotron x-rays, directional information can be obtained and used to determine precipitate orientation and size. In this case, the structure is the same for electric vector polarization in the sample surface regardless of the plane studied, but differs considerably normal to the surface plane. The graph on the lower right shows models of EXAFS Fourier transforms for different types of precipitate clusters. Only sub nanometer particles of hematite-like structure yield agreement with the observed polarized data (Waychunas et al. 1999). This and other observations suggest that sorption occurs preferentially at step edges. Drying later aggregates the sorbed complexes and induces nucleation of highly oriented precipitates. The nature of the edges and steps appear to be more important than the actual type of surface plane in controlling these reactions (Waychunas et al. 2002). These types of nanoprecipitates dramatically alter the further reaction properties of the quartz surface.

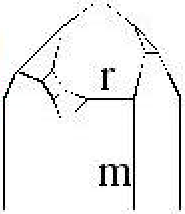
Waychunas, GA, Davis JA and Reitmeyer, R (1999) GIXAFS study of Fe^{3+} soprtion and precipitation on natural quartz surfaces. J. Synchrotron Rad. 6, 615-617

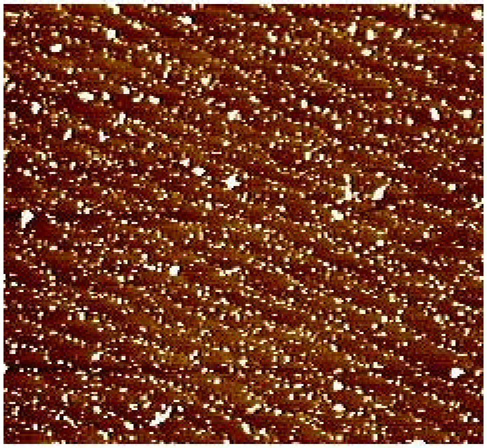
Waychunas, GA (2002) Grazing Incidence X-ray absorption and emission spectroscopy. Reviews in Mineralogy and Geochemistry Vol. 50 (in press).

Waychunas GA, Davis JA, Reitmeyer R, Vivet D, White A (2002) (in preparation).

Fe^{3+} precipitation on quartz

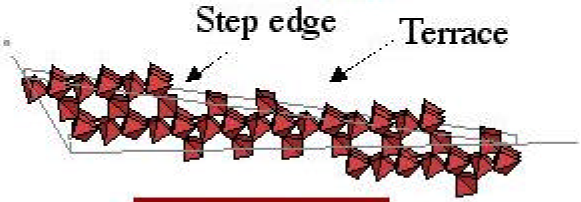
GI-XAFS and AFM



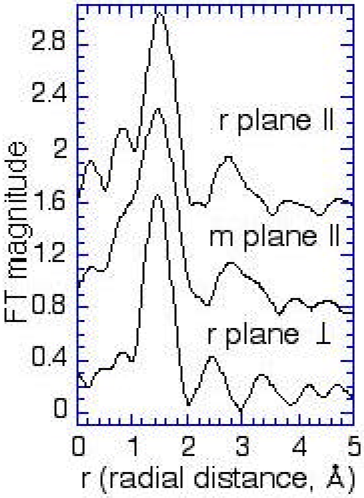


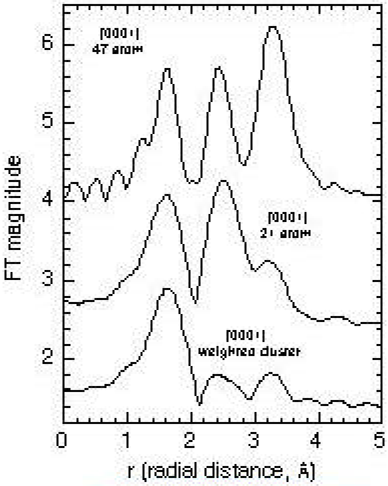
Polymers tend to occupy Step edges

r (10-11) and m (10-10) are the commonest quartz surface planes.



Quartz m plane model

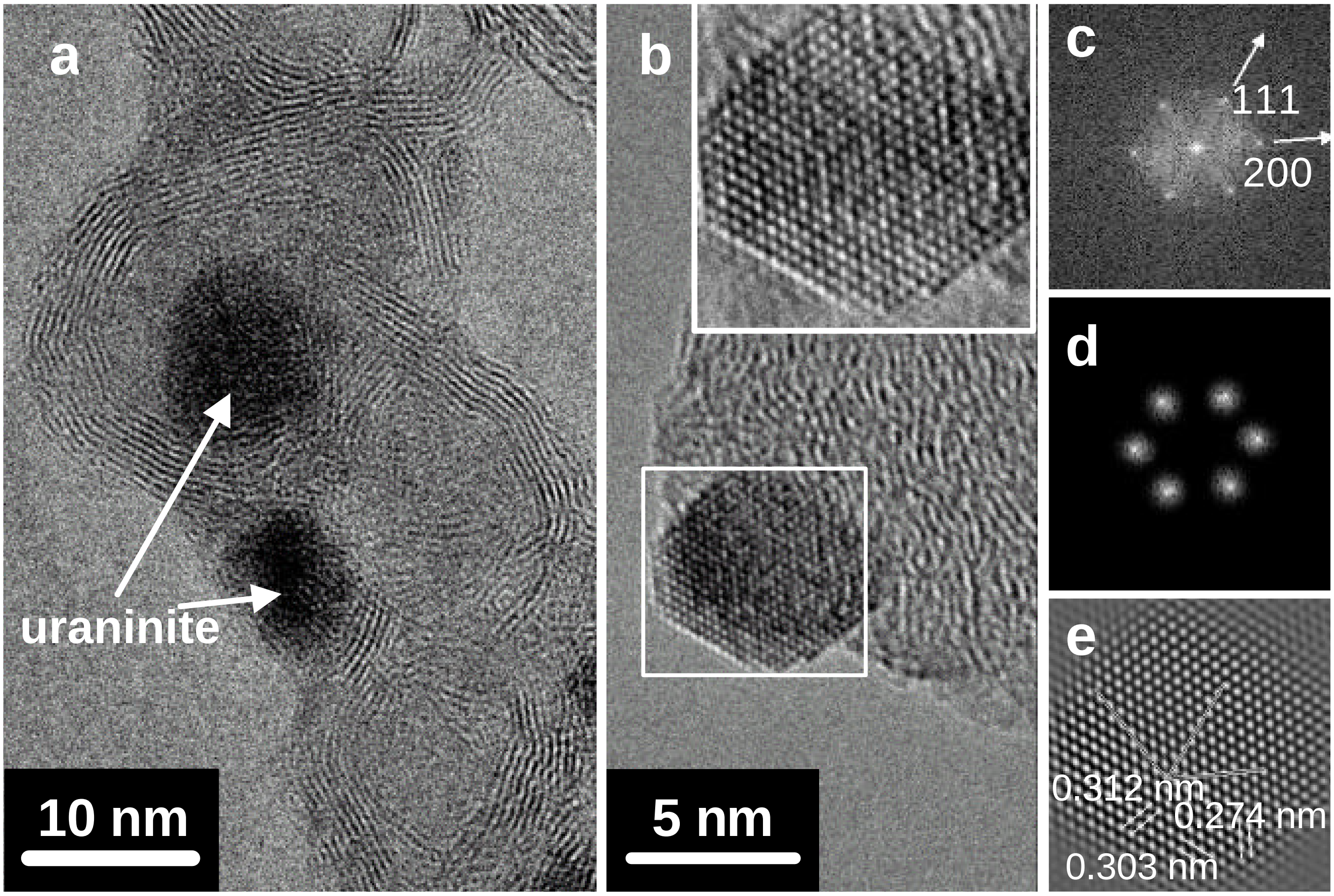




Experimental results for different quartz surfaces and polarizations

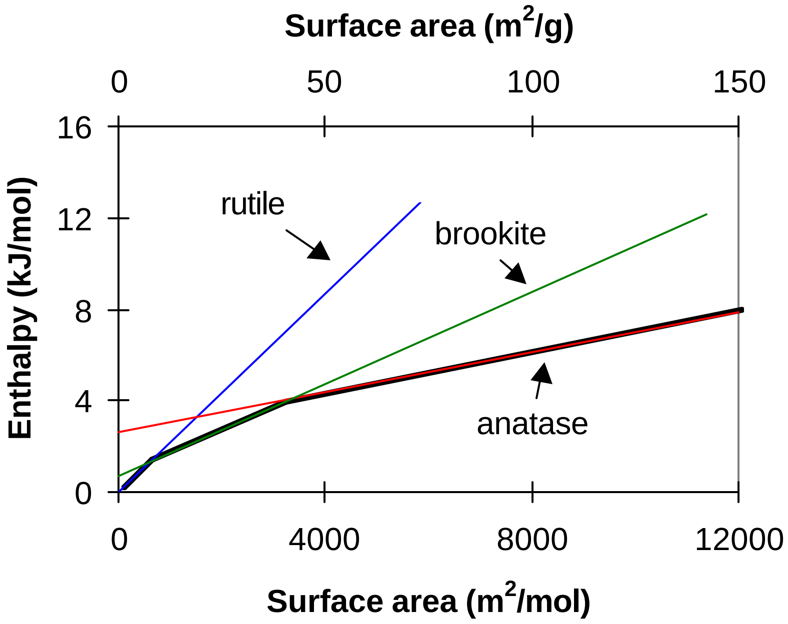
Polarized GI-XAS allows determination of precipitate size (0.9 nm)

3.2 Uraninite nanocrystals in carbonaceous particles in the atmosphere



There is increasing concern for the health effects of fine particles (less than a micron) inhaled from polluted air. Aerosols collected from Detroit contain very small amounts of uranium. Due to these extremely low concentrations (< 10 ppm), the form of the uranium has been unknown. We identified nanocrystals of uraninite, UO_{2+x}, encapsulated in carbonaceous matter (about 50 nm) with a structure similar to that of fullerene. (a) HRTEM image of U-bearing nanoparticles encapsulated in a "cage" of fulleroid. (b) HRTEM of the U-particle. The matrix carbon has lost its structure because of the focused electron. The inset is the Wiener-filtered image of the area outlined by the white square. In the Fast Fourier Transformed (FFT) image (c), the main diffraction maxima were selected (d) and a reverse FFT completed to produce a clear image (e). The lattice spacing in three directions can be determined and the diffraction spots (c) can be indexed as those of uraninite. The "carbon-caged" nanocrystals of uraninite are protected from the immediate oxidation that would lead to increased mobility of uranium in the environment. Still, the presence of uranium in the very fine fraction of atmospheric particulates provides another pathway for radiation exposure. (S. Utsunomiya and R. C. Ewing, submitted (2002) to Environmental Science & Technology)

3.3 Phase stability crossovers in nanophase oxides



Enthalpy, relative to bulk rutile, of nanophase titania polymorphs, measured by high temperature oxide melt calorimetry.

Fine-grained oxides precipitated from aqueous solution often crystallize in structures different from those of coarsely crystalline materials: ?-alumina instead of corundum, anatase and brookite instead of rutile, maghemite instead of hematite, and a host of complex hydrous iron oxyhydroxides. It has been suspected that differences in surface energy stabilize, as nanoparticles, polymorphs that are metastable in the bulk. High temperature oxide melt solution calorimetry directly confirmed this enthalpy crossover for ?- versus ? - alumina (McHale et al. 1997) and for anatase and brookite relative to rutile (Ranade et al. 2002). Relative to bulk rutile, bulk brookite is 0.71 ± 0.38 kJ/mol and bulk anatase is 2.61 ± 0.41 kJ/mol higher in enthalpy. The surface enthalpies of rutile, brookite, and anatase are 2.2 ± 0.2 J/m^2, 1.0 ± 0.2 J/m^2, and 0.4 ± 0.1 J/m^2 respectively. The closely balanced energetics directly confirm the crossover in stability of nanophase TiO_2 polymorphs inferred by Zhang and Banfield (1998). The heavy lines in the figure show the energetically stable phases as a function of surface area.

J. M. McHale, A. Auroux, A. J. Perrotta, and A. Navrotsky (1997) Surface energies and thermodynamic phase stability in nanocrystalline aluminas, Science 277, 788-791

M.R. Ranade, A. Navrotsky, H.Z. Zhang, J.F. Banfield, S.H. Elder, A. Zaban, P.H. Borse, S.K. Kulkarni, G.S. Doran, and H.J. Whitfield (2002) Energetics of nanocrystalline TiO_2 Proc. Nat. Acad. Sci. 99, suppl 2, 6476-6481

H. Zhang and J.F. Banfield (1998) Thermodynamic analysis of phase stability of nanocrystalline titania. J. Mater. Chem. 8, 2073-2076

3.4 Nanoscale Bacterial Protein Layers

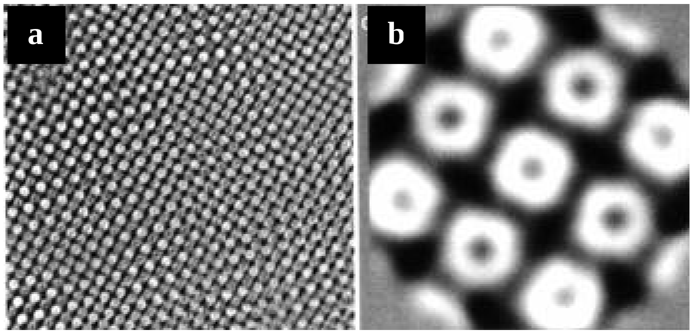
While humans are newcomers to the field of nanoscale science, prokaryotes long ago mastered the art of synthesizing fully functional nanoscale structures and utilizing properties that exist only at the nanoscale. Today most of the 10^{30} prokaryotic cells on Earth exist in close association with mineralogical components in soil and subsurface environments (Whitman et al., 1998). It is here within the geologic womb of nature that prebiotic molecules formed on mineral surfaces and developed into single celled organisms. Since then bacterial life and evolution have been tightly coupled to mineralogical processes, since minerals provide the raw materials for life (e.g., minerals are a source of nutrients and participate in energy generating reactions). Billions of years of evolutionary selection have allowed bacteria to tailor macromolecules (e.g., lipids, proteins and polysaccharides) for the express purpose of uniting cellular processes with minerals surfaces (e.g., adhesion, electron transfer, or biomineralization reactions). Recent experiments suggest that the intimacy between the biological and geophysical worlds is preserved in the genetic make-up of microorganisms such that there is a natural affinity or specificity between bacterially produced macromolecules and minerals. Lower et al. are using force microscopy to quantify the natural, inter- and intra-molecular forces between bacterially produced biopolymers and mineral surfaces (Lower et al., 2000; 2001b). Force measurements have revealed that dissimilatory metal reducing bacteria command exquisite control of protein synthesis such that specific outer membrane proteins are produced to mediate contact with iron hydroxides as opposed to aluminum hydroxide isostructures (Lower et al., 2001a). This information is being used to create a lithographic technique in which a living cell is induced to fabricate various biomolecular patterns on inorganic surfaces, thereby creating nanoscale domains of different structures and functions (see figure, below).

Lower S. K., Hochella M. F., and Beveridge T. J. (2001a) Bacterial recognition of mineral surfaces. Nanoscale interactions between *Shewanella* and ?-FeOOH. *Science* **292**, 1360-1363.

Lower S. K., Tadanier C. J., and Hochella M. F. (2000) Measuring interfacial and adhesion forces between bacteria and mineral surfaces with biological force microscopy. *Geochimica et Cosmochimica Acta* **64**, 3133-3139.

Lower S. K., Tadanier C. J., and Hochella M. F. (2001b) Dynamics of the mineral-microbe interface: Use of biological force microscopy in biogeochemistry and geomicrobiology. *Geomicrobiology Journal* **18**, 63-76.

Whitman W. B., Coleman D. C., and Wiebe W. J. (1998) Prokaryotes: The unseen majority. *Proceedings of the National Academy of Sciences* **95**, 6578-6583.



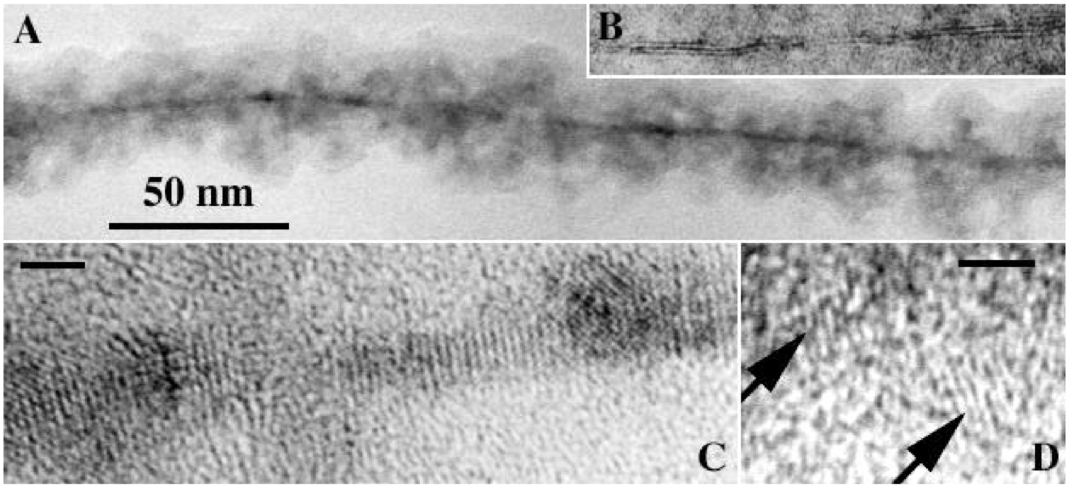
Bacteria produce paracrystalline protein layers on their outer surfaces. The ones shown here have center-to-center spacing between donuts of 11 nm (b is higher resolution of a). A fundamental goal is to understand how cells modulate intermolecular forces of interaction between these biopolymers and nascent minerals such that bacteria control the growth or dissolution of select mineral phases. Images courtesy of T. Beveridge.

3.5 Biologically Produced Iron Oxyhydroxide Nanoparticles

Recent investigations have explored nanoscale interactions between microbially-produced polymers and iron oxyhydroxides. Banfield et al. (2000) and Nesterova et al. (in review) used transmission electron microscopy to study polymer biomineralization reactions in the environment. Borrowing principles learned from these analyses, they synthesized similar nanocrystalline iron hydroxide materials in the laboratory using self-organizing biopolymers as templates for mineral growth (Nesterova et al., 2002). They showed that iron oxyhydroxide nanoparticles assemble and epitactically grow on polysaccharide substrates. This mineralization reaction generates very large aspect ratio crystals of a normally metastable polymorph. In addition to the biomimetics relevance of work of this type, biomineral and inorganic precipitation products can be compared to establish criteria to evaluate the biogenicity of ancient Earth and extraplanetary materials.

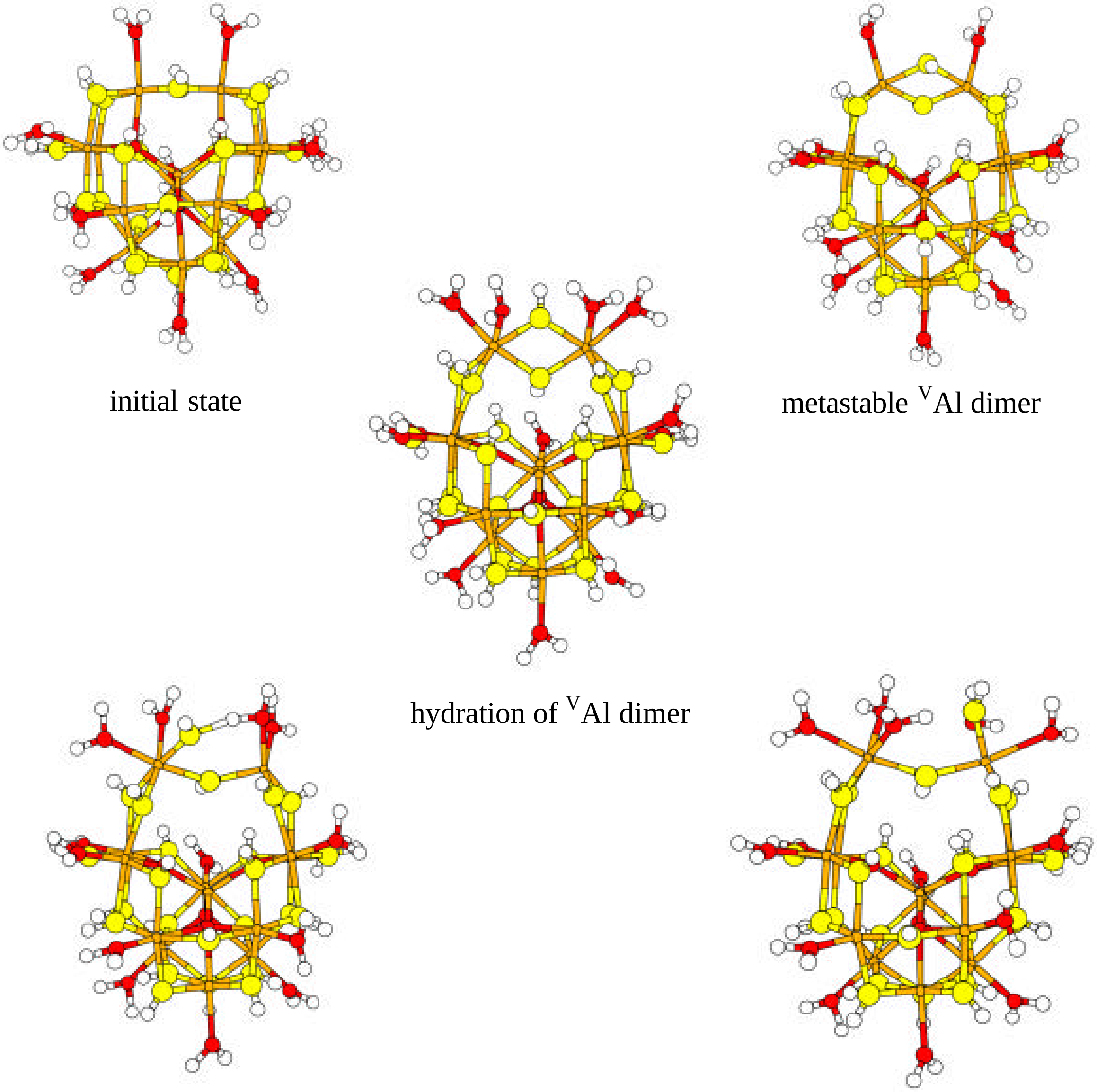
Nesterova, M., Moreau, J., and Banfield, J.F., A Biomimetic approach to mineralization of carbohydrate polymer templates by FeOOH. Geochim. Cosmochim. Acta., in press.

Nesterova, M., Chan, C.S., Welch, S.A., and Banfield, J.F. Biomimetic synthesis of filamentous hybrid nanomaterials. Nature, in review.



High-resolution transmission electron microscope images of mineralized polymers (A) associated with bacteria. One elongate (up to 1000:1:1 aspect ratio) pseudo-single crystal core of akaganeite (B, C) only a few nanometers wide always develops along the polymer fibril (dark line in A and enlarged in B). Aggregates of 2-3 nm diameter ferrihydrite (D) coat the mineralized polymer strand. Large aspect ratio akaganeite crystals can be synthesized using an biomimetic approach based on these observations. Scale bars in C and D are 2 nm.

3.6 Molecular clusters as models for nanoparticles: experiment and simulation



initial state

hydration of ^{V}Al dimer

metastable ^{V}Al dimer

? ? OH bond dissociation

2nd hydration

Snapshots from a molecular-dynamics simulation of ?-AlAl$_{12}$ (AlO$_4$Al$_{12}$(OH)$_{24}$(H$_2$O)$_{12}^{7+}$) (Al$_{13}$) in aqueous solution; (solvent waters are eliminated for clarity). Metal ions are the small brown atoms, hydroxide ions are the large yellow atoms, water molecules and ?$_4$-O ions are red.

Large aqueous molecules, such as Al$_2$O$_8$Al$_{28}$(OH)$_{56}$(H$_2$O)$_{24}^{18+}$ (Al$_{30}$) and AlO$_4$Al$_{12}$(OH)$_{24}$(H$_2$O)$_{12}^{7+}$ (Al$_{13}$) help develop models to predict chemistry in the shallow

Earth. Such molecules are sufficiently small that their reactions can be studied directly by solution spectroscopic methods not applicable to colloids and the results compared with simulations. The results are surprising, both *in vitro* and *in computo*. In the Al_{30} species, experiments show that the rates of exchange of oxygens in hydroxyl bridges are enormously sensitive to small changes in structure, yet the rates of exchange of bound waters differ by a factor of only ?5 and fall into the same range as aluminum monomers (Casey and Phillips 2001). The hydroxyl bridges at the surface of these large molecules exchange many times with the aqueous solution before the molecule itself dissolves; in other words, the outer parts of the molecule are constantly exchanging isotopes with the bulk solution. The highly coordinated oxygens in the center of the molecule control the dissolution rates and not the more-conspicuous hydroxyl bridges (Casey et al., 2000).

The figure shows snapshots of molecular dynamics simulations of water and hydroxide exchange on ? $l_{??}$?in aqueous solution (Rustad and Casey 2002)). A five-coordinated aluminum (^{V}Al) in the outer part of the molecule is key to exchange. Hydroxide exchange is governed by a metastable state that involves dissociation of two O-^{VI}Al bonds and the formation of a dimeric subunit (top right complex). This metastable state may become hydrated, returning the ^{V}Al to ^{VI}Al (middle complex). Dehydration returns the complex to the initial state with the possibility of exchanging water molecules. Alternatively, the $?_{?}?$OH between the ^{VI}Al ions may dissociate, again creating ^{V}Al. Additional hydration of the ^{V}Al converts one of the bridging $?_{?}?$OH groups into a bridging $H_3O_2^-$ (bottom right) with a shared proton that is free to exchange between the each oxygen in the $H_3O_2^-$ bridge. This mechanism explains why there are two exchange rates for $?_{?}?$OH in Al_{13} molecules: only the $?_{?}?$OH that bridge aluminum atoms attached to *different* $?_4$O atoms are reactive. Furthermore, the simulation shows why putting different metals into the *M* position affect reactivity. The $?_4$-O is more weakly polarized in the longer Ga-$?_4$O bond and has it has a decreased tendency to dissociate in the ^{IV}Ga-?$?_4$O -^{VI}Al bridge than for the ^{IV}Al-?$?_4$O -^{VI}Al bridge.

Casey, W. H., Phillips, B. L., Karlsson, M., Nordin, S., Nordin, J. P., Sullivan, D. J., and Neugebauer-Crawford, S. (2000) Rates and mechanisms of oxygen exchanges between sites in the $AlO_4Al_{12}(OH)_{24}(H_2O)_{12}{}^{7+}$(aq) complex and water: Implications for mineral surface chemistry. *Geochim. Cosmochim. Acta* **64**, 2951-2964.

Casey, W. H. and Phillips, B. L. (2001). The kinetics of oxygen exchange between sites in the $GaO_4Al_{12}(OH)_{24}(H_2O)_{12}{}^{7+}$(aq) molecule and aqueous solution. *Geochim.* Cosmochim. Acta **65**, 705-714.

Casey W. H., Phillips B.L., and Furrer G. (2001) "Aqueous aluminum polynuclear complexes and nanoclusters: a review," in (J.F. Banfield and A. Navrotsky, eds), *Nanoparticles and the Environment*, Reviews in Mineralogy and Geochemistry **44**:167-190.

Rustad, J. R. and Casey W. H. (2002) Molecular dynamics simulation of hydroxide and water exchange mechanisms in a model $MO_4Al_{12}(OH)_{24}(H_2O)_{12}{}^{7+}$ compound. Geochemical Transactions (submitted).

4. Relevance to National Needs

4.1 Environmental Safety, Homeland Security, and Human Health

The storage of nuclear waste is a contentious national and international issue. Safe stewardship on a timescale of thousands of years is essential. Nanoparticles provide experimental models and data for the next generation of trustworthy computer simulations to predict the safety of geologic storage of radioactive and other waste. Nanoclusters are small enough for simulation of chemical interactions using the current generation of computational methods, which are generally limited to a few tens to a few hundred atoms and picoseconds of reaction time. Furthermore, pollutant transport by nanoparticles (colloids) may be crucial but is poorly known at present. By comparing predictions with experiments on nanoparticles, we can assess the accuracy of predictions about reactivity in the Earth and refine the models. These predictions are increasingly important as the nation asks Earth scientists to help safeguard human health and to provide expert understanding of the geochemistry resulting from pollution and from assaults on national security.

National needs include ensuring the quality, abundance and safety of the water supply, and monitoring and improving air quality. The generation and chemistry of fine atmospheric particulates, under conditions of changing industry and changing climate, are not clear. Particulates in the atmosphere, including nanoparticles, play a role in degrading human respiratory health and the need to understand them is particularly compelling now that the threat of radioactive fallout from a 'dirty bomb' is real. Particulates, as soot and minerals, carry the radioactivity and even normal nonradioactive particulates transport metal and organic pollutants. Many scenarios of biological warfare and bioterrorism invoke the transport of biological agents (e.g. anthrax spores) through the atmosphere. Understanding such transport requires the integration of understanding of different phenomena on many different length scales, from chemical understanding of adhesion at nanoparticle surfaces, to photochemistry, to particle agglomeration, to global transport.

The transport rates of aqueous nanoparticles, including nanoparticles of actinide elements, is not understood and the movement of these particles may indicate a key vector for distributing contaminants from a waste repository to the biosphere. Similar considerations apply to toxic metals, organic pollutants, and bacteria and viruses, including materials intentionally introduced into water supplies. Here nanoscale geochemistry must be integrated with hydrology and microbiology.

4.2 Environmentally Friendly Manufacturing

The nation needs to reduce the environmental damage caused by manufacturing and to continue decreasing manufacturing costs. Because reactivity increases and surface forces and surface modification become increasingly important as particle size decreases, research in nanoparticle geochemistry could lead to new methods of material synthesis that eliminate toxic organic solvents and minimize expensive high-temperature processing. The syntheses may involve aqueous or benign solvents. Understanding natural systems may provide new insight into benign manufacturing through geomimetic and biomimetic strategies. The small size of nanoparticles is key because the relative influence of directed chemical bonding and nonspecific solvation forces can be controlled through choice of the particle size, surface and the solvent conditions. Even structural phase transformations of monodisperse small particles that are otherwise unfavored have been induced by treatment with an appropriate solvent.

4.3 Mining: Minerals, Oil, and Gas.

The extraction of solid, liquid, and gaseous resources from the Earth requires new technology and these developments will be driven by issues of both environmental safety and lower cost. Nanoparticles play a prominent role in aqueous-leaching processes, which increasingly replace the roasting of sulfide ores. Acid-mine drainage, the legacy of mining sulfide ore bodies, is associated with extensive nanoparticle and microbiological transport of heavy metals. Nanoparticles and fine-grained sediments play a major role in permeability of oil reservoirs. Gas hydrates are a major possible future source of natural gas and a problem in Arctic oil pipelines. The formation and decomposition of these clathrates, with zeolite-like frameworks, may be dominated by nanoscale phenomena, including catalysis by surface-active molecules. Understanding and controlling these processes will have major economic impact and it must be remembered that large reserves of precious metals, like gold, are held as nanoparticles in the matrix of rocks (e.g., Carlin-type gold deposits).

4.4 New Geomimetic Materials: from Optoelectronics to Pharmaceuticals

New crystalline polymorphs can be stabilized at the nanoscale by controlling the interplay between bulk and surface forces. These polymorphs have unique chemical properties so that they can serve as new types of catalysts and electronic materials. Nanoparticles and nanocomposites may form the basis for a new generation of robust sensors that can be employed in homeland security. Natural materials (manganese oxides, clays, sulfides, complex silicates, inorganic-organic composites analogous to those in soils) need to be explored as models or actual materials for such applications. The lack of a center of symmetry in many complex mineral structures makes them potential candidates, in the bulk and at the nanoscale, for many nonlinear optical, ferroelectric, and other applications.

Earth materials already make robust consumer products and we need to explore the potential for nanoparticles to extend these uses. Materials, for examples clays and zeolites, are already used in essential steps in the synthesis of pharmaceutical products as catalysts, reagents and as vaccine adjuvants. Better understanding of the role of these nanophase natural materials may lead to new materials for drug delivery and pharmaceuticals. Biomineralization, an intrinsically nanoscale process, is key to the success of bone and tooth replacement materials and other implants.

4.5 Ecosystem Stability and Climate Change

Nanoparticles may be essential to ecosystem productivity in the upper ocean and the chemistry of the atmosphere. An example of the magnitude of this issue is that dust from the Gobi Desert in China may lead to algal blooms in the Pacific Ocean by providing a critical supply of micronutrients. Modulation of dust fluxes to the oceans has been postulated to affect global marine productivity, with profound consequences for climate. These particles are certainly important to the chemistry of the upper atmosphere, where even such key processes as the cycling of water are affected by atmospheric particle size and chemistry.

4.6 Agriculture and Food

Nanoparticles are critical to the productivity of soils, controlling water and nutrient transport and eliminating pollution. Soil conditioners, feed additives, even kitty litter, are dominated by natural nanomaterials and zeolitic materials are used to absorb nitrogen contamination in livestock feedlots. The textures and taste of food are controlled by the state of aggregation of water, fat, starch, sugar, and protein. Natural nanoparticles are often added to control such aggregation, for example sodium aluminosilicates in coffee creamer powder.

5. The Unique Skills, Contributions, and Viewpoint of Earth Scientists

The Earth is a chemical reactor that has been conducting synthesis experiments involving the whole periodic table of elements and using heat, pressure, time, and living organisms for up to 4.5 billion years. In this sense, the Earth has already explored the range of possible structures and conditions over geologic time and geoscientists are familiar with the products of these processes. Geoscientists can draw upon this knowledge for identifying new useful materials, possible processes, and likely environmental problems.

Earth scientists have polished the skills needed to understand the Earth's synthesis conditions, to identify and characterize the products, and to reproduce the experiment on the laboratory scale. Furthermore, geochemists have skills in aqueous chemistry, in the systematics of stable-isotope distributions, in thermodynamic analysis of complicated assemblages, and in analytical chemistry that are unmatched by other disciplines. Geoscientists have pioneered the use of both stable and radiogenic isotopes as a sensitive probe of the properties of materials and record of past geologic and environmental events. Mineralogists continue pioneering modern structural analysis of complex minerals, tiny crystals, and disordered solids by conventional x-ray, synchrotron x-ray, neutron, and spectroscopic techniques. The geoscience community is very active in the design and operation of equipment at synchrotron beamlines and is taking advantage of improved neutron facilities at LANSCE at LANL and the future SNS at ORNL.

Geoscientists have a broad knowledge of natural materials in their vast array of structures and compositions and are extending this knowledge to examine the ways in which microbes create novel and amazing chemistries in small vesicles. Geoscientists are comfortable with immense scales of time, distance and chemical conditions, and have developed experimental methods to attain extraordinarily high temperatures and pressures. These skills make them unique among researchers concerned with minerals and structures and the fate of substances in the Earth.

6.0 Scientific Needs

A fundamental goal of the Nanogeoscience community is to understand the properties of nanoparticles that change disproportionately with size and distinguish them from those that simply scale with surface area. We must then understand how both the enhanced surface reactivity and the unique nanoscale properties affect geologic processes. A related subject is to describe the chemistry of very small pores of nanometric dimension and understand how they influence the integral chemistry of the Earth.

Two examples illustrate the geologic application of fundamental nanoscale science. The catalytic properties of zeolites relate to how their nanopores constrain the reactants and it is likely that nanopores in sediments and rocks have analogous unique chemistries that we do not yet understand. In oxides developed for magnetic memories and other applications, the ability to maintain magnetization over time decreases as the particle size diminishes. For materials science applications such as compact discs, the concern is about stability of magnetic memory over months to decades. In paleomagnetism, the concern is on a time scale of millions of years.

The growing nanogeoscience community needs access to specialized techniques and samples and better coordination of scientific and educational activities. Specifically, the following needs are identified.

6.1 Shared Facilities and Expertise

We need to establish resources that can serve an emerging nanogeoscience community of about 200 scientists (roughly twice the number attending the workshop) and their students. These resources are of two sorts: major facilities such as synchrotron and neutron beams and specialized but smaller-scale facilities. Though the former have well-established mechanisms for access, the latter are scattered around the community and generally are specialized research tools in individual research laboratories. Nevertheless, they require an expense, expertise, and infrastructure which cannot and should not be duplicated in every laboratory. Furthermore, methods which are fairly routine for bulk materials, for example x-ray diffraction and vibrational spectroscopy, require extra care and modification when used for nanoparticles. In summary, tools to characterize nanomaterials are not uniformly dispersed among the Geoscience community and some are not even represented.

A related issue is that, even when equipment is available, and increasingly computerized and user-friendly, the ability to use it to its full potential and to interpret data wisely requires experience and a grasp of basic physical and chemical principles that new users do not always possess. The lack of familiarity with a new method presents an undesirable barrier to progress in this field. Thus, the availability of equipment and educational issues are intimately linked, see below.

We need access to a suite of techniques that explore matter at the nanoscale. These include:

?? Transmission electron microscopy (TEM) and electron beam spectroscopic and analytical methods
?? Scanning electron microscopy (SEM) and associated analytical techniques
?? Atomic force microscopy (AFM), scanning tunneling microscopy (STM), and other probe microscopies
?? Solid state and solution nuclear magnetic resonance (NMR) spectroscopy
?? Thermal analysis: thermogravimetry, differential scanning calorimetry, evolved gas analysis
?? Solution calorimetry

?? X-ray diffraction (XRD), including analysis of very small samples
?? Isotopic measurements
?? Mössbauer spectroscopy
?? Ultraviolet, visible, infrared, and Raman spectroscopy, with special handling issues for nanoparticles

At major national facilities (synchrotron and neutron sources), the following capabilities are critical to nanogeoscience:

?? Extended x-ray absorption fine structure (EXAFS), X-ray absorption near edge structure (XANES), and related x-ray spectroscopies, including those suitable for light elements
?? Spatially resolved chemical and isotopic analytical techniques
?? Diffraction and small angle scattering methods
?? Synchrotron-based infrared spectroscopy

We need to complement experiments with computer simulation of processes across a large range of scales. Access to computational facilities and interaction of experimentalists and theorists is critical.

New users need help from expert collaborators. Sophisticated techniques are not "black boxes" that can be used in turnkey operations. Rather, the planning and execution of experiments and the interpretation of results require depth of experience and knowledge, often in fields (condensed mater physics, for example) which are not part of normal geoscience training. We strive to have all members of the community expert in one method of nanomaterial characterization, to have moderate understanding of one or two other methods, and to be generally familiar with many.

6.2 Reference Materials

We need to identify, synthesize, and disseminate reference nanoparticle and porous materials, since the few such existing materials are neither readily available nor necessarily geologically relevant. Complementary experiments performed on such uniform reference materials will provide valuable data for both experimentalists and theorists. To accomplish this goal, we need methods of synthesizing large amounts of monodisperse nanoparticles and nanoporous solids, which are difficult to handle and have chemically unique properties. These needs are similar to those of the materials science community and we anticipate synergy with them. However, our materials are different and "dirtier" and we anticipate reluctance in the materials community to allow the synthesis of geonanomaterials for fear of contamination of rigidly controlled synthesis environments. We need to identify specialized facilities (ion-beam deposition, molecular-beam epitaxy, etc.) that would be useful to the needs of the geoscience community.

6.3 New Methods for Manipulating Small Samples

Geoscientists need to develop techniques to conduct direct experiments at the micro- to nanoscale by manipulating nanoparticles directly. Technologies developed in Microscopic Electro-Mechanical Systems (MEMS) and optical tweezers may be applicable. Manipulating atoms and molecules on surfaces by using AFM tips is another avenue. These advances provide geoscientists with the technology to conduct experiments at the micro- and nanoscale by manipulating directly the properties of a surface. Atomic-scale manipulations provide information that has previously been unattainable (e.g., desorption energetics at specific surface sites). Particularly important are experiments that probe the mineral – microbe interface. Can Earth scientists employ biochips to sort materials? How do we make very delicate machines sufficiently robust to withstand harsh conditions and geologic materials? Can such robust sensors provide monitoring for environmental processes and detection of environmental accidents and terrorist acts?

6.4 Isolating Nanoclusters from Solution

Presently the properties of solution-state clusters are largely inferred and not determined directly. In chemistry, small clusters are isolated for structural characterization by special choice of solvents and sometimes by design and synthesis of special ligands, which can be synthesized *de novo* specifically for separating a molecule. The tools of inorganic, organic, and protein chemistry are useful for geoscientists, but few of us yet have these skills, nor have they been traditionally valued by the geoscience community. The skills of synthetic chemistry must be transferred to the community of nanogeoscientists if we are to advance beyond deriving inferences about nanoparticle chemistry to direct demonstration of their essential features.

6.5 *In Situ* Methods of Characterizing Nanoclusters and Nanopores

We need methods to count clusters in natural waters and in the atmosphere that do not modify the essential chemistry. These methods must apply to particles of sizes smaller than can be studied by conventional light scattering. These sampling methods may require ultraclean laboratories and new methods of sampling atmospheric and aqueous particles. Bulk methods of filtration destroy the essential chemistry of these particles. An urgent need also exists for an understanding of the properties of nanoscale pores since interfacial reactivity is strongly influenced by the size, interconnectivity and shape of the pore.

6.6 Large Scale Experiments and Field Trials

Geoscientists are responsible for predicting the chemistry of materials in the Earth. We need field studies to understand how nanoparticles move in natural porous media. Numerous investigators are studying transport in porous media, but it is not clear that the macroscopic conceptual framework remains valid at these very small sizes where physical properties are less important than chemical properties. Better communication between those examining the chemical properties of nanoparticles and those studying their physical transport is essential.

The important questions are fundamental in nature: How does filtration theory apply to nanoparticles that are on the same size scale as solutes? How do fine surface precipitates detach from a substrate once formed? Atmospheric scientists assume that a nanoparticle, once adsorbed to a larger particle, will remain trapped forever because of Van der Waals forces. Is the same true for aggregates in aqueous solutions or in particles with very low fractal dimensions?

6.7 Integration with Geomicrobiology

Microorganisms create and destroy nanoparticles and use them as an energy source or to detoxify their environment. The evidence for these subtle manipulations is profound in the geologic record. For example, some of the earliest forms of respiration are believed to have relied on the transfer of electrons between proteins on the surface of a bacterium and iron oxyhydroxides. These interactions are mediated by complex proteins and other organic compounds, often existing in biofilms, at the surfaces of rocks and minerals.

Our objectives must be to examine the natural affinity between biopolymers and mineral surfaces, to understand how inter- and intra-molecular forces direct the formation of nanocrystals on the surface of biopolymers; to understand how microorganisms modulate their interactions with mineral surfaces; and to use this information to create biogeomimetic materials with novel properties.

Advances in nanoscale science and technology enable the study of interaction of organic/biological molecules with mineral surfaces. Important areas of study include:

?? bacterial adhesion – biomolecules or functional groups involved in adhesion reactions which bind microorganisms to nanparticles and mineral surfaces

?? biomineralization – role of biomolecules, biopolymers, functional groups on bacteria as templates that direct mineral nucleation and/or growth; development and growth of metastable phases.

?? electron transfer reactions and enzyme mediated dissolution – how a protein shuttles electrons to a mineral; how this electron transfer affects sorption and dissolution of metals or other contaminants .

?? biofilm formation – understanding processes at both molecular and physiological level

?? biogeomimetics - harnessing and scaling up these processes for materials synthesis, bioremediation, medical implants, and other applications

6.8 Molecular Modeling

Molecular modeling methods are especially valuable in nanoscale problems because of their ability to tie together experiments in aqueous chemistry, high vacuum surface science, crystal chemistry, calorimetry, and a variety of spectroscopies. Computational methods can be very effective in bringing together what may be otherwise isolated measurements. Simulations are currently limited by feasible length and time scales and the accuracy and flexibility of the representation of the atomic interaction potentials. There is an urgent need for more research in effective ways to represent interatomic interactions, particularly in aqueous systems. Research and technology transfer (from the chemistry, physics, and material science communities) is also needed in long-time and large-system molecular dynamics methods, including hybrid methods which consider coarse-grained and finely detailed levels of atomic interactions simultaneously.

Nanoscale computer simulation methods are also limited by the difficulty of "virtual sample preparation". Because of the length and time scales involved in nanoscale simulation, results are often strongly dependent on initial conditions. It is necessary to be able to quickly and intelligently construct initial conditions for simulations of nanogeochemical processes, so that the model systems are relevant and so that the dependence of the results on the initial conditions can be assessed as easily as possible.

7.0 Synergy of Nanogeoscience with Existing and Future Programs

Geoscientists must organize themselves within the large and growing national nanoscience and nanotechnology initiatives. During the first month of the 21st Century, the National Nanotechnology Initiative (http://www.nano.gov/) was established under the auspices of the National Science and Technology Council's Committee on Technology. A new publication of the National Research Council, "Small Wonders, Endless Frontiers: A Review of the National Nanotechnology Initiative" can be read on-line at (http://www.nap.edu/catalog/10395.html?onpi_topnews_061002)

The Clinton Administration had proposed to double the Nation's investment in nanotechnology to reach a grand total of $495 million. Although Congress did not approve the proposed budget in its entirety, the National Science Foundation's nanotechnology budget in 2001 increased by fifty percent over its level in 2000. This unprecedented growth has continued. President Bush's 2003 FY budget (http://www.nano.gov/2003budget.html) proposes an expenditure of $710 million, a 17% increase over the 2002 FY. This investment has led to major programs in nanomaterials and nanotechnologies at National Science Foundation, Department of Energy, National Aeronautics and Space Administration, Department of Defense, Environmental Protection Agency, and National Institutes of Standards and Technology, as well as the Departments of Agriculture, Transportation and Justice. Under the Defense program, 16 MURI (Major University Research Instrumentation) nanoscience projects were created as part of the Defense University Research Initiative on Nanotechnology (DURINT).

In the Department of Energy, fundamental research will be increased in three areas: synthesis and processing, condensed matter physics and catalysis (http://www.sc.doe.gov/production/bes/BESAC/PPT11-14-01.htm). The first three (ultimately five) centers have already been initiated: the Molecular Foundry at Lawrence Berkeley National Laboratory, the Center for Nanophase Materials Sciences at Oak Ridge National Laboratory and the Center for Integrated Nanotechnology at Sandia National Laboratories and Los Alamos National Laboratory. Geoscientists must articulate their needs for using these facilities to characterize environmental nanomaterials. A key point is that the natural evolution in understanding of environmental toxicity and chemistry lies at the molecular scale where information on nanomaterials can lead to disproportionate breakthroughs in understanding. This point is implicitly recognized by the DOE through establishment of molecular-scale research programs (e.g., the Environmental Molecular Science Laboratory (EMSL) at Pacific Northwest National Laboratories). Computational nanoscience has strong overlap with the DOE ASCI (Accelerated Scientific Computing Initiative) program.

The EPA has issued a second STAR solicitation in four research areas in nanotechnology: Green manufacturing and processing, remediation and treatment, sensors and environmental implications of nanotechnology. The NSF has two major programs: Nanoscale Interdisciplinary Research Teams and a Nanoscale Exploratory Research program.

The NSF is drafting a 10 year research agenda in environmental science (http://www.nsf.gov/geo/ere/ereweb/ACERE/_10_year_agenda_DRAFT,html). There is tremendous confluence in the ideas, needs, and priorities expressed there and in this report.

This massive infusion of support has resulted in a tremendous increase in the amount research and educational activity on nanomaterials and nanotechnologies. Special sessions and symposia on these topics are now common at the annual meetings of the Materials Research Society, American Physical Society, American Chemical Society, American Geophysical Union and the Geological Society of America, as well as at Gordon Conferences and NATO workshops. Indeed, entire issues of journals, such as *Science, Proceedings of the National Academy of Sciences,* and the *Materials Research Society Bulletin,* have been devoted to nanomaterials.

The Geoscience community needs to articulate the point that nanoscience research has an immense impact on our understanding of chemistry and geologic process in the shallow Earth because it is inherently molecular. These nanoscale processes are central to our understanding of soil formation, global cycling of elements, ocean productivity, environmental safety and biogeochemistry.

8.0 Education and Human Resources

8.1 Graduate Education

Modern geoscience is a combination of field observation, laboratory work, and modeling. A professional must be well versed in at least one of these aspects and conversant with all. This intermingling of theory, experiment, and observation is especially important in nanogeoscience because of the molecular control of processes at the nanoscale. Graduate education must emphasize this point.

Geoscience has evolved from a discipline that mainly served extractive industries (oil, gas, minerals) to a field having a broader, but perhaps less focused, impact on many societal issues. Geoscientists are evolving to be much more quantitative in their predictions and physical science oriented in their outlook. This evolution has not been uniform across the field of Geoscience, but is led by researchers who are taking a molecular view of reactions in the Earth. The overall community is grappling with this identity crisis that is coupled to declining interest in the sciences among American students. These factors have led to a significant decline in the numbers, and perhaps the quality, of doctoral students trained exclusively in the Geosciences. Some geoscience programs have thrived, however, by drawing students from other disciplines (e.g., Chemistry, Toxicology, Soil Science, Materials Science, Civil and Environmental Engineering) who clearly see the connection between Earth materials and environmental problems and are motivated by the desire to be directly useful in solving society's needs. New emerging fields like nanogeoscience, coupled with the post Sept. 11th world, are an expression of this interdisciplinary vigor and herald an opportunity to continue this trend. Geoscience is being reinvigorated through research on modern problems. The multidisciplinary aspects of nanogeoscience provides unique educational challenges. Many of the techniques and concepts needed to work at this scale are too specialized be covered in traditional coursework. Highly multidisciplinary research requires greater use of hands-on workshops or internships.

The NSF IGERT (Integrative Graduate Education and Research Traineeship) or DOE User-Facility are possible models. Already, a number of IGERTs actually or potentially contain elements of nanogeoscience. These include:

?? Oregon State University: "*The Earth's Subsurface Biosphere: Coupling of Microbial, Geophysical, and Geochemical Processes*"
?? Pennsylvania State University: "*Biogeochemical Initiative for Education*"
?? University of Alabama - Tuscaloosa: "*Freshwater Graduate Studies Integrating Ecology, Hydrology, and Geochemistry in Regions with Contrasting Climates*"
?? University of California at Davis: "*Nanophases in the Environment, Agriculture, and Technology*"
?? University of Michigan- Ann Arbor: "*Biosphere-Atmosphere Research and Training*"
?? University of Washington: "*Astrobiology: Life in and Beyond Earth's Solar System*"
?? University of Wisconsin-Madison: "*The Human Dimensions of Social and Aquatic Systems Interactions*"

These programs have new interdisciplinary courses. Students are co-advised in their Ph.D. research by scientists from several disciplines, and we have found that active recruitment and mentoring attract excellent American students. Graduate education in nanogeoscience, whether or not within an IGERT, can benefit from these strategies.

As discussed above, applying specialized techniques requires both equipment and expertise. Nanogeoscience needs a coordinated effort which will:

?? Make specialized facilities accessible, provide the infrastructure to make them user-friendly, and provide expertise to help with designing experiments and interpreting results.
?? Provide workshops and courses in both the basic scientific concepts and hands on experience in the use of specialized methodologies
?? Encourage students, postdocs, and faculty to ask, and be able to answer, "*What tools do I need to solve this problem and where can I find them?*" rather than "*What problem can I solve with tools I have available here at home?*"

We need to identify novel career paths for our students and closer integration with industry and federal laboratories can achieve this goal. Experience in unconventional Geoscience departments has shown that students who are well trained in the molecular concepts of nanogeoscience, and in Earth and Environmental Science as well, are highly employable in a wide variety of positions in the private and public sector. Molecular concepts are important because they are needed to understand the disequilibrium reactions that control modern (as opposed to ancient) geochemistry. The national laboratories, in particular, have a need for well-trained American graduate students who can work on a number of intrinsically interdisciplinary problems related to national security. This point needs to be recognized and publicized within the Geoscience community.

8.2 Outreach

Because of the extensive societal ramifications of nanogeoscience, we have a duty to interact with the public, with regulatory agencies, and with policy makers. Often regulatory decisions (for example the definition of "asbestos", the PM5 standard for air pollution particulates, drinking water standards) are made with little understanding of the science. As part of the larger need for a scientifically literate populace, we need to interact at many levels to educate and inform. Because of the time and effort it takes to interact well, we need to do this as an organized community and not on an *ad hoc* basis.

To improve the flow of bright students into science in general, and nanogeoscience in particular, we need interactions with undergraduates, K-12 students, and their teachers. Some of the more innovative successes of outreach in the Science and Technology Centers and MRSECs of NSF may provide models. Once more, such efforts are more effective and efficient, when pursued by the community as a whole. Perhaps the most fruitful way to influence science education is via the Schools of Education at various universities.

9. A Distributed Center for Nanogeoscience

The above considerations led naturally in the workshop to a discussion of the possibility of creating a community-wide organization of nanogeoscientists. A distributed center, linking various research groups, rather than one at a single location, was favored. Features of such a center would include:

?? Improved accessibility to and infrastructure for specialized facilities
?? Workshops and courses for both fundamental scientific concepts and instrument use
?? Mechanisms for visits of students and postdocs to different institutions
?? Development of new tools and capabilities
?? A forum for continuing discussion of scientific issues and priorities
?? Interfacing with government and industry
?? Outreach to science educators both within and outside the universities

Although the workshop did not have time to come to a definite recommendation, let alone a specific plan, for such a center, many of us sense a strong need to proceed strongly and quickly in that direction. Several people suggested that the CHiPR and COMPRES initiatives could be a model for such a center. We view with great interest the imminent announcement from NSF of the FY 2003 Nanoscale Science and Engineering Program, which is to contain a call for Center proposals. There are likely to be other opportunities for us as well.

Such a center would complement and enhance the effectiveness of much needed additional funding for individual and small group projects in nanogeoscience. A first-order budgetary estimate of needed funding would be, per year

?? Center for Nanogeoscience \$2.5M
?? University single investigator and small group projects \$2.5M
?? Federal lab nanogeoscience projects \$2.5M (plus continuing support for synchrotron and neutron facilities)

Appendix 1

Nanogeoscience workshop: working groups and schedule (6/09/02)

Working groups

nanomineralogy (formation, structure and reactivity of natural nanoparticle systems)
Bish (leader), Kirkpatrick, Veblen, Huang, Banfield, Finnegan (scribe), Manceau, Kalinichev, Criscenti
Breakout room: Perseverence Hall

nanoparticle stability (thermodynamics, kinetics of formation, aggregation)
Navrotsky (leader); Meakin; Luther; Schoonen; Alivisatos, Vayssieres, Zhang, Gilbert
Breakout room: Perseverence Hall addition

nanoparticle geochemistry and transport (aerosols; liquid phase transport; cycling of species from continents to oceans; role in geochemical cycles)
Casey (leader); Lunden; Sparks; Martin; Bishop; Lam (scribe); Guay; Cole, Moridis, Sonnenthal
Breakout room: Building 70A 3377

nanoparticle-organic/biological reactions and interplay; biomimetics
Lower (leader); Maurice; Holman; Rosso; O'Day; Banfield; Phelps; Hazen
Breakout room: Building 2 room 100B

nanomaterials properties; purpose-designed nanogeomaterials and applications
Rustad (leader); Murad; Kim, Sposito, Diallo; Halley; Myneni, Penn, Brown
Breakout room: Building 50 Auditorium

relationship of nanogeoscience to other nanoscience programs and efforts (materials science, chemistry, chemical engineering, colloid chemistry; microbiology); nanogeoscience facilities
Ewing (leader); Redden; Zack; Baer; Ridley, Waychunas, Shuh, Traina
Breakout room: 70-191

Facilitators (moving from group to group)
Waychunas, Banfield

Scribes (students-helping with information transfer and note taking)
Mike Finnegan, Phoebe Lam, David Edwards

Workshop Schedule

Friday June 14 [all talks in building 50 auditorium]

Welcome (**Pier Oddone** Deputy Director LBNL) 8:30
Workshop Charge (**Alexandra Navrotsky**) 8:35-8:50
Workshop Logistics (**Glenn Waychunas**)

Formation and stability of nanomaterials

(**Navrotsky**: Thermodynamics of nanomaterials) 8:50-9:10
(**Alivisatos**: Synthesis strategy for semiconductor nanomaterials) 9:10-9:30
(**Vayssieres**: Aqueous growth and stability of nanostructured oxides and hydroxides) 9:30-9:50

Nanoclusters in aqueous solution

(**Casey**: Aqueous oxide molecular clusters) 9:50-10:10
(**Luther**: Soluble molecular clusters-precursors to nanocrystalline materials) 10:10-10:30

Discussion on nanoparticle formation and stability 10:30-10:50

Nanomineralogy

(**Penn**: Nanoparticle growth mechanisms: Size, shape and microstructure) 10:50-11:10
(**Bish**: Towards a quantitative understanding of surface properties of natural nanomaterials) 11:10-11:30
(**Veblen**: TEM and chemical imaging of geological nanomaterials) 11:30-11:50
(**Ewing**: Radiation-induced nanophase formation: What can we learn from nature?) 11:50-12:10

Discussion on nanomineralogy 12:10-12:30

Lunch 12:30-1:30

Perspectives from Agency representatives 1:30-1:50

Rachel Craig, NSF
Barbara Ransom, ACS/PRF
Nora Savage, EPA
Henry Shaw, DOE BES
Linda Veblen, NRC

Nanomaterials and surfaces

(**Waychunas**: What can we learn from bulk surfaces that applies to nanoparticle surfaces?) 1:50-2:10
(**Sparks**: Metal sorption on soil mineral surfaces) 2:10-2:30
(**Myneni**: organic molecule interactions on mineral surfaces) 2:30-2:50
(**Schoonen**: Metal sulfides: Surface chemistry, stability, reactivity and size effects.) 2:50-3:10

Discussion nanomaterials and surfaces 3:10-3:30

Nanoparticle aggregation and transport

(**Meakin**: aggregation of nanoparticles and colloids) 3:30-3:50
(**Cole**: Structure and dynamics of fluids in confined geometries) 3:50-4:10
(**Moridis**: colloid transport modeling for the Yucca Mountain project) 4:10-4:30

Discussion nanoparticle aggregation/transport 4:30-4:50

Saturday June 15 [all talks in building 50 auditorium]

Nanoparticles in the environment

(**O'Day**: Nanoscience and hydrothermal systems) 8:30-8:50
(**Manceau**: Nature and reactivity of soil nanoparticles) 8:50-9:10
(**Lam**: Colloids in the upper oceans) 9:10-9:30
(**Bishop**: Martian particulates) 9:30-9:50
(**Martin**: Atmospheric particulates) 9:50-10:10

Discussion nanoparticles in various environmental regimes 10:10-10:30

Simulation of nanoparticles

(**Rustad**: Topics in simulation strategies for oxide nanoparticles) 10:30-10:50
(**Halley**: Modeling atomic and electronic structure of nanoparticles of geochemical interest) 10:50-11:10
(**Criscenti**: Metal-anion pairing at Oxide/water interfaces) 11:10-11:30
(**Zhang**: Molecular dynamics study of structure and stability of 2nm ZnS nanoparticles) 11:30-11:50

Discussion Simulation of nanoparticles 11:50-12:10

Lunch 12:10-1:10

Microbe-nanoparticle interactions

(**Banfield**: enzymatic nanoparticle formation) 1:10-1:30
(**Phelps**: Precipitation of metal oxides and doped magnetites by microorganisms) 1:30-1:50
(**Holman**: Cr reducing bacteria: in situ studies with synchrotron-based microFTIR) 1:50-2:10
(**Rosso**: Non-local bacterial electron transfer to hematite surfaces) 2:10-2:30

Discussion: Microbe-nanoparticle interactions 2:30-2:50

Breakout of working groups 2:50

Discussions among working groups 2:50-5:00

Writing of group reports 5:00-6:40

Sunday June 16 [working group leaders only; 70A-3317A]

Presentation of group reports 8:30-9:30

Writing of final reports from all groups 9:30-12:30

Appendix 2

ATTENDANCE LIST FOR NANOGEOSCIENCE WORKSHOP

June 14-16, 2002

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