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## There's plenty of room at the bottom: Nanoscience in geochemistry

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**Abstract**—Nanoscience is a relatively new field of research that primarily involves the discovery and exploration of the properties of matter in the size range of roughly one to 100 nanometers, the so-called nanoscale. Mechanical, electrical, thermodynamic, and other types of properties are strongly modified as the physical dimensions of a material enters the nanoscale, and researchers in the field are just beginning to catalog and understand these property modifications in this fuzzy area between the classical (bulk) and quantum domains. It is also becoming more and more apparent that many earth materials exist in the nanodomain as minute particles or thin films, especially in low-temperature environments, but also in mid- to high temperature environments. As examples, this article describes how nanoscience has started to be applied to mineral weathering, mineral-bacteria interaction, and metal transport in acid mine drainage systems, but this is only the beginning. The future directions of nanoscience in geochemistry will include a determination of the identity, distribution, and properties of nanosized particles in aqueous and soil systems, thin films in both low and high temperature systems, and nanosized features on mineral surfaces. *Copyright © 2002 Elsevier Science Ltd*

### 1. INTRODUCTION

This article is an expanded version of the Geochemical Society's presidential address that I delivered at the Eleventh Annual Goldschmidt Conference in Hot Springs, Virginia, USA, on May 21, 2001. The subject was, and is, the emerging field of nanoscience within geochemistry. It is not my intent to write a review, but rather to give a perspective of this field shaped by 15 years of personal experience. What follows contains a mix of history, pure science, application, and projections, all aspects of nanoscience that in my view drive this field and are responsible for making it a forefront research area in geochemistry. Finally, I hope that this article is useful (for different reasons) to experts in the field, as well as to those unfamiliar with it. I wrote it with that intent.

The first point is a bold one. Along with the current revolution in biology and the health-related sciences, the revolution that we are presently witnessing in nanoscience and technology probably holds the greatest potential in shaping the world of the future. This point has been well justified and documented (Lowndes, 2000; Roco, 1999; Roco et al., 2000). Governments and industries worldwide have clearly recognized this situation, especially over the last decade, and they are investing billions of dollars in a concerted effort to capitalize on this field both in the near and long-term. How the earth sciences and geochemistry in particular will ride this rapidly cresting wave is, in part, what this article is about.

Nanoscience is typically defined (for good reason, as we shall see later) to be relevant between one nanometer ( $10^{-9}$  meters, or 10 Angstroms) and a few tens to perhaps one hundred nanometers. But with the advent of X-rays, crystallographers were working at the nanometer scale, and smaller, nearly 90 years ago (the Braggs solved the first crystal structures in 1912). But scientific historians do not point to the

beginnings of nanoscience and technology until 1959, the year that Richard Feynman, a quantum physicist and one of the 20<sup>th</sup> century's greatest scientists, gave a speech to the American Physical Society entitled "There's Plenty of Room at the Bottom" (e.g., see Sykes, 1994). Feynman was fascinated by the notion of scaling, and in this speech, he imagined that a single bit of information could be stored in a nanospace (specifically a 125 atom cluster), an exceptionally bold prediction at that time. At that scale of miniaturization, he estimated that all books in the history of the world could be stored within a cube 0.2 mm on a side (and thus his lecture title). His genius was not this, but his realization that "all things do not simply scale down in proportion," a point that is discussed below and is now considered the hallmark of nanoscience. What he was predicting was that as one scaled things down into the nanometer scale, materials would behave differently, and that this could be made into an advantage. His brilliantly insightful points at that time can best be summarized by another quote taken directly from his lecture: "This field is not quite the same as the others [fields of physics] in that it will not tell us much of fundamental physics. . . , but it is more like solid-state physics in the sense that it might tell us much of great interest about the strange phenomena that occur in complex situations." It is now clear that both today and in the future, nanoscience will provide a great deal of information on unraveling scientific models of complex situations.

Nanoscience and nanotechnology have grown exponentially over the last decade or so, helped in large part by the invention of the scanning tunneling microscope by Gerd Binnig and Heinrich Rohrer at IBM's research center in Zurich. But even long before that, manipulation of matter in the nanoscale had a world-changing influence. I think the best example of previously established nanotechnology (although it wasn't called this at the time), and a field that has great as-yet unrealized potential in the earth sciences, is heterogeneous catalysis. Although this technology helps lead a multi-trillion dollar chem-

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ical industry worldwide, the way in which most modern heterogeneous catalysts work had never been fully understood. This is starting to change as researchers realize that critical explanations will come from nanoscience. It turns out that many of these surface-mediated catalytic reactions take place on nano-sized particles or surface features that have the ability to trigger reactions due to properties specific to the nanodomain. This realization holds the promise of promoting a new revolution in this field.

So, what is it about this part of physical dimensional scale that makes it so special? How can we use knowledge gained in this area to advance the earth and environmental sciences on a local, regional, or even global basis? We will start by gaining perspective and an appreciation for the nanoscale within the context of both earth and universal dimensional scales, and then proceed to answer the specific questions just raised.

## 2. THE CONTEXT OF NANO: THE DIMENSIONAL UNIVERSE

Everyone knows that the universe is vast, but few stop to think that its vastness may cover more than 60 orders of dimensional space (Fig. 1a). In outer space, the distance to the farthest galaxies from Earth is approximately  $10^{26}$  m (i.e., 10 billion light-years). In inner space, the size of fundamental particles, such as leptons (electrons are in this family) and quarks are not known from experiment, but we do know that they are less than  $10^{-18}$  m in dimension. We can only get an idea of the size of the smallest fundamental particles from models. The grand unified theories of forces predict the existence of exceptionally small particles, called X bosons, with a size in the vicinity of  $10^{-30}$  m. In string theory, which attempts to unify the four forces in nature (strong and weak nuclear, electromagnetic, and gravitational), elementary particles are modeled not as points but as one-dimensional strings with a length of only  $10^{-35}$  m. Clearly, although difficult to visualize, inner space seems to be as vast, or more so, than outer space.

Within this range of dimension, from the size of the universe down to the size of the elementary particles that make up the universe, the range of scale that encapsulates the earth sciences pales in comparison (Figs. 1a,b). Merely 17 orders of magnitude are covered from atomic to earth dimension. Nevertheless, geoscience disciplines neatly cover this range of scales, from whole earth seismologists and geochemists to crystallographers. And as in physics, represented at both ends of its dimensional realm with astrophysicists and elementary particle physicists, one part of the scale is no more vital than another. It is just as important in the long run to understand quarks as it is galaxies, and in the earth sciences, minerals as it is oceans. Perhaps science is most novel and exciting when effective bridges can be made between stops along this dimensional road. An excellent example in physics involves the formation of a neutron star via production of neutrons from proton/electron collisions (the so-called inverse  $\beta$ -decay nuclear reaction, understood at the scale of nuclear particles, or  $10^{-15}$  m):



In the final stages of the neutron star core collapse, a supernova results. The entire outer envelope of the star is blown into interstellar space forming expanding gas rings. Such rings have

been observed at  $10^{16}$  m in diameter as they continue to expand. Therefore, the results of this single nuclear reaction are expressed in excess of 30 orders of magnitude in dimensional space, roughly twice the dimensional range of the earth sciences. Yet observing only the small or large-scale would result in very limited understanding of the process and its importance/consequences. The earth sciences have many scaled-down equivalents, for example the fundamental chemical processes by which ozone is formed and destroyed, coupled to its distribution in our atmosphere and its effect on mean earth temperature, an example that clearly covers the entire earth science dimensional realm. And as in all cases, understanding the whole depends on understanding the parts.

## 3. THE NANOSCALE: WHAT'S THE BIG DEAL?

The portion of the dimensional scale relevant to nanoscience, as briefly mentioned in the Introduction of this article, spans approximately two orders of magnitude, from  $10^{-9}$  to  $10^{-7}$  m (see Fig. 1b), a bit of dimensional space that I will refer to as the nanoscale or nanodomain. These dimensions first conjure up images of molecules, from relatively small ones up to macromolecules. Although molecular chemistry (and in our case, molecular geochemistry) is certainly a part of nanoscience, it is only a relatively small part of the entire field. Any solid, fluid, or space in the dimensional realm of the nanoscale is a part of nanoscience, and subject to its peculiarities.

Before stating any of the underlying principles of nanoscience, it would be prudent to give an actual example of one of them. A particularly illustrative example that most readers would already have at least conceptual familiarity with involves taking two aluminum wires with an electrical potential between them, and gently touching them together. Naturally, a current will flow from one wire to the other. However, the surface of the wires are not conductive aluminum as one might assume, but in fact alumina ( $\text{Al}_2\text{O}_3$ ) due to air exposure. Certainly, bulk alumina (whether in an amorphous state or crystalline, e.g., corundum) has a wide band-gap and is a classic insulator. Why doesn't the alumina, ubiquitous on the surface of normal aluminum wire, stop the flow of electrons from one wire to the other? The answer lies in the physical dimension of the alumina coating. The coatings on the aluminum wires are very thin, typically on the order of one nanometer, clearly in the nanoscale range of dimension. The mean free path of electrons in oxides, that is the mean distance that an electron can travel without undergoing an energy loss event, is also on the nanometer scale, although the exact mean free path depends on the electron energy. Therefore, electrons travelling through the conduction band of the aluminum wire will suddenly find themselves in the normally unoccupied conduction band of the alumina, but unimpeded because it is likely that the width of the alumina is less than or similar to their mean free path in that material. In other words, just due to the dimensions and geometry of the alumina, it effectively behaves more like a conductor than an insulator, and good electrical contact between the two wires is the result. Although something we take for granted, or in fact were never aware of in the first place, this is a dramatic result. One simply needs to imagine what electronics would be like if bulk properties also applied to thin films.

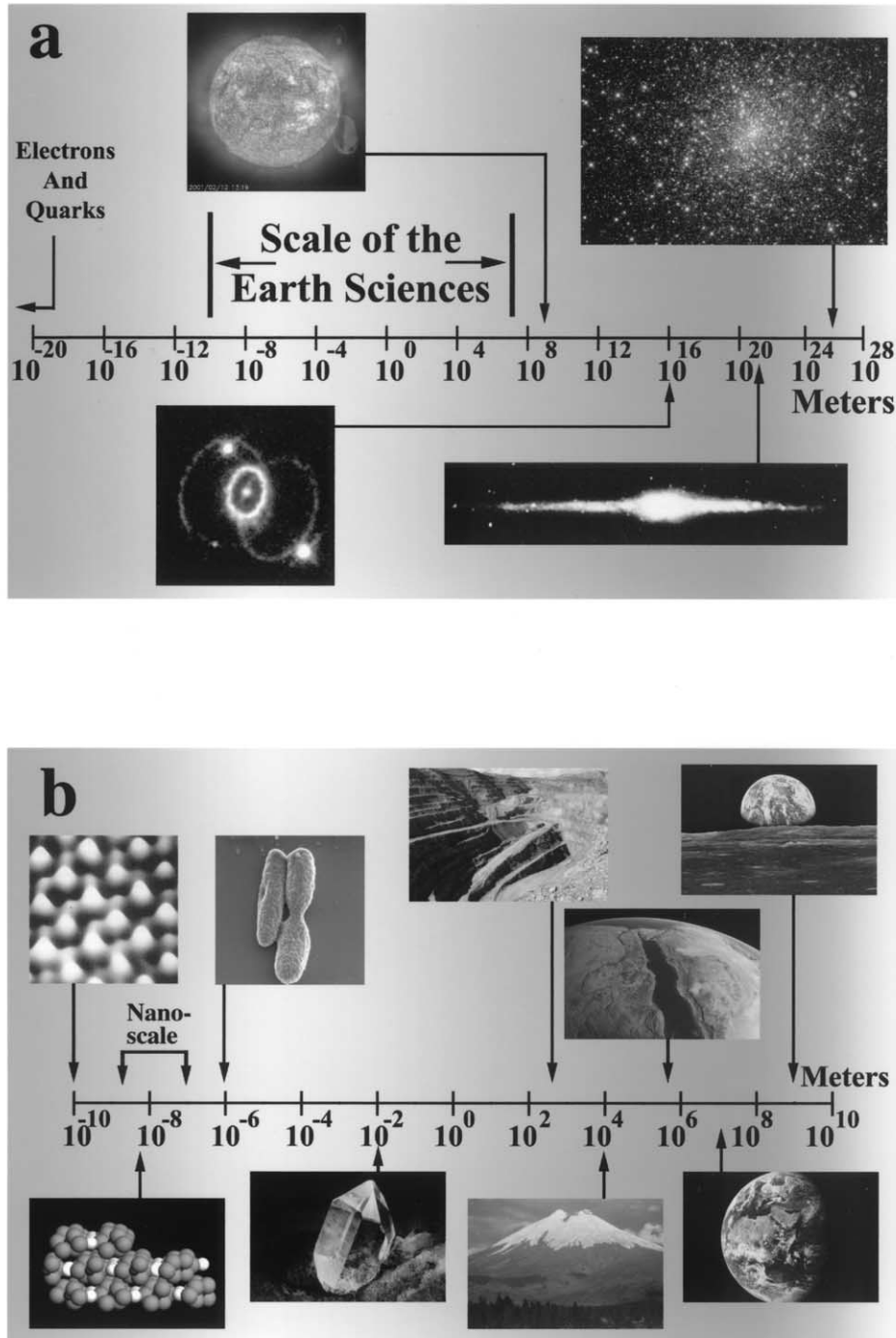


Fig. 1. (a) The known dimensional scale of the universe. On the small end, fundamental particles such as electrons and quarks are smaller than  $10^{-18}$  m, and may approach  $10^{-30}$  m in size or smaller, but such dimensions are not physically measurable at least at this time. Other stops depicted along this dimensional journey include: the scale of the solid earth sciences, from atoms ( $10^{-10}$  m to  $10^7$  m); the Sun ( $10^9$  m in diameter) as seen from the Extreme UV Imaging Telescope on the SOHO satellite; expanding gas rings ( $10^{16}$  m in diameter) from supernova SN1987a as observed by the Hubble Space Telescope; infrared image of the inner portion of our own galaxy (the Milky Way is nearly  $10^{21}$  m in diameter); and distant galaxies (the most distant are  $10^{26}$  m away). (b) The dimensional scale of the earth sciences. Stops depicted along this dimensional journey include: scanning tunneling microscope image of lead and sulfur atoms on a galena surface (atomic size  $10^{-10}$  m); crystallization nucleus of calcite ( $10^{-9}$ – $10^{-8}$  m); bacterial cells ( $10^{-6}$  m in length); a single crystal of quartz ( $10^{-2}$  m); a typical open pit mine (the Carlin Mine in Nevada, USA,  $10^2$ – $10^3$  m); Mt. Fuji, Japan, a composite volcano ( $10^4$  m); the Red Sea from space ( $10^5$  m wide and  $10^6$  m long); Earth ( $10^7$  m); the Earth-Moon system as seen from Apollo 11 ( $4 \times 10^8$  m).

This simple scenario is a great example of the importance of nanoscience, and the promise of nanotechnology. As stated in Richard Feynman's lecture and implied in this example, nanoscience is based on the premise that materials properties in the bulk do not simply scale into the nanodomain, but property modification, and in some cases entirely different properties, are to be expected.

An underlying principle of nanoscience that encapsulates our example can now be stated. As the size of a material approaches a length or dimension associated with a property of that material, that property will begin to change. As the material size passes below that length/dimension, the property will be strongly modified. In our example, the oxide coating on the aluminum wires still has the composition of bulk alumina, and even the same atomic structure (except for the interfacial and surface layers), but due to its nanoscale dimensions, it does not behave like bulk alumina anymore. In the nanoscale size range, physical, electrical, magnetic, thermal, kinetic, and other properties can be altered dramatically simply due to the physical dimensions of the material.

#### 4. NANOSCIENCE IN GEOCHEMISTRY

As the importance of nanoscience becomes clearly recognized, more and more earth scientists are looking back at past research in a new light, starting new research programs, and generally taking an inventory of nanosized earth materials discovered and identified to date. Finding nanosized particles in nature using a transmission electron or scanning probe microscope is no longer a curiosity. It may in fact be the key to the physical and/or chemical machinery of an entire geochemical process, perhaps equivalent to, and just as important as, the relationship between reaction (1) above and a supernova, although of course covering a smaller range of dimensional space.

Where do nanosized materials exist on Earth? As best we can tell at the moment, they seem to be ubiquitous in low temperature earth environments (weathering, soil-forming, and surface and ground-water environments). In high temperature environments, where the kinetics of grain coarsening is rapid, and away from the influence of biologic processes, nanoscience should be less influential. However, there are still vitally important issues such as nucleation and earliest growth of grains in igneous and metamorphic rocks, and the presence of thin films between grains in rocks (e.g., Watson, 1999, on fluid movement along grain boundaries; and Mogk and Mathez, 2000, on thin carbonaceous films in rocks). At intermediate temperatures, Gribb and Banfield (1997) and Penn and Banfield (1999a, 1999b) have recently shown nanoscale mechanisms that control the transformation of anatase to rutile under hydrothermal conditions. To me, these studies clearly demonstrate that nanogeoscience in mid to high-temperature regimes will be very profitable in the future. Nevertheless, I will restrict the discussion below to low-temperature environments.

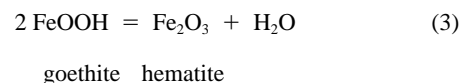
Two studies that caught my eye years ago, in that they realized the importance of the nanoscale in the earth sciences long before this terminology was invented and the field came into vogue, are Stöber and Arnold (1961) and Langmuir (1971). Even today, I think that these early studies are excellent examples of the importance of nanoprocesses in geochemistry.

Stöber and Arnold (1961) is a paper about, among other things, the enhanced solubility of minute quartz fragments (in fact in the nanodomain) adhering to micron-sized grains of dry-ground quartz. This is a relatively early experimental mineral dissolution study that recognized the importance of enhanced solubility of extremely fine grains relative to coarse particles. This phenomenon has been described in a modified version of the Kelvin equation which relates the solubility of a material to its surface free energy and grain size (e.g., Adamson, 1982):

$$\frac{S}{S_0} = \exp\left[\frac{2\gamma\bar{V}}{RTr}\right] \quad (2)$$

where  $S$  is the solubility (in mol/kg  $H_2O$ ) of grains with inscribed radius  $r$  in meters,  $S_0$  is the solubility of the bulk material,  $\gamma$  is the surface free energy in  $mJ/m^2$  (see, e.g., Parks, 1984, 1990, for discussions of surface free energy),  $\bar{V}$  is the molar volume in  $m^3/mol$ ,  $R$  is the gas constant in  $mJ/mol\cdot K$ , and  $T$  is the temperature in  $K$ . The equation says that as the grain dimension decreases, the solubility of that grain will go up exponentially relative to the measured solubility of a very large grain ( $S_0$ , where the grain size has no appreciable effect on solubility). Considering the surface free energy of oxides and silicates and their molar volumes, the solubility only begins to change appreciably as the radius of a particle gets very small, that is down to the nanoscale. Stöber and Arnold (1961) argued, along with other authors after them (e.g., Holdren and Berner, 1979; Petrovich, 1981), that this same phenomenon is responsible for the increased solubility of sharp, minute features on mineral surfaces.

Langmuir (1971) concerns the particle size effect on the goethite to hematite reaction:



Based on the measurements of heats of solution of goethite and hematite as a function of total surface area per mole of material by Ferrier (1966), Langmuir calculated the  $\Delta G^\circ_{298}$  of reaction of the goethite to hematite transformation as a function of particle size down to the nanometer level. He concluded that coarse goethite (grains larger than 1 micron) was stable relative to coarse hematite in water up to  $\sim 80^\circ C$  and 1 atm. He further concluded that with grains of hematite and goethite of approximately equal size, goethite would be thermodynamically more stable above a grain size for both of 0.08 microns (i.e., 80 nm), and hematite would be more stable below this grain size. Also, when hematite is coarse grained and goethite fine, goethite would be more stable above a grain size of 0.15 microns (i.e., 150 nm), and hematite stable when goethite was below this grain size. These calculations of Langmuir have been refined by a more recent analysis (Diakonov et al., 1994).

Before leaving this subject, although Langmuir (1971) is instructive as an early example of nanoscience in geochemistry, the formation of goethite and hematite in nature, at least in soils, is a great deal more complicated than implied by the above (e.g., Cornell and Schwertmann, 1996, and many references therein). Even if only equilibrium conditions are considered, the relative stability of these two important phases must

also depend on at least water activity as well as chemical impurities. In nonequilibrium conditions, kinetics will also play a major role, tied in with other factors like organic/biologic influences. In reality, goethite is by far the most common iron oxide in soils, either forming directly or transforming from less stable ferrihydrite. Hematite is currently thought to most commonly form from the precursor ferrihydrite, but generally under warmer and dryer conditions than would be favorable for goethite formation from ferrihydrite. Nevertheless, the Langmuir (1971) paper is still an excellent example of an early study that recognized the importance of nanoscience, as we know it today, in geochemistry.

## 5. EXAMPLES OF NANOSCIENCE IN THE CRITICAL ZONE

This section contains examples of nanogeoscience that involve the “critical zone” of the Earth. The critical zone, as defined in a National Research Council book entitled “Basic Research Opportunities in Earth Science” (Jordan, 2001), is the place where the land meets the fluid envelopes of the Earth, that is the hydrosphere and atmosphere. It is the place where we live, and it is the place that provides us with fresh water, agriculture, and many vital natural resources such as timber and most mineral deposits. Considering all the geo- and bio-aspects of this zone, it is probably the most heterogeneous and complex portion of the entire Earth, yet understanding it relatively well is certainly important in intelligently sustaining this planet for human habitation.

Earth processes within the critical zone can be conveniently divided into four principal and overarching categories based on the physical, geochemical, and biologic processes that occur there. All of these categories are strongly cross-linked, each one affecting the others to various degrees. They are 1) biologic activity, which, due to organism nutritional requirements, drives a significant amount of the chemical cycling within and between water, soil, rocks, and the atmosphere; 2) weathering, which is constantly at work in the critical zone, generating soil, destroying and producing minerals in the process, and redistributing elements among water, rocks, and organic materials; 3) fluid transport, the critical component in water resources supply and management, as well as everything from flooding to landform development; and 4) near-surface tectonics, shaping the land surface through faulting, subsidence, uplift, and mass movement. It is not surprising that nanoprocessees play some role, and often a key role, in all four categories in the critical zone. Below, I will describe a few of these.

### 5.1. Water/Rock/Bacteria Nanoscience

Although by no means developed, nearly all aspects (both geo- and bioprocesses) of weathering, soil, and water/rock interaction science are inexorably linked to nanoscience. Within the Earth’s near-surface, materials that are broken down, as well as materials that are produced, are often in the nanoscale regime. Further, as organic molecules, simple and complex, as well as bacteria and all flora and fauna in soils and rocks interact with the mineral components present, nanodimensions and nanoscale processes are the order of the day. If one does not know what is going on at this scale (and generally

we do not), one can by no means have the complete picture of these exceptionally complex systems.

The biggest scientific problem is that one needs to know how things work at this small and awkward scale in the first place. The reason that one needs to know this is because processes that occur at the micron and larger dimensions simply do not scale down to the nanoscale. Within the nanoscale, as we have seen above, entirely different processes are possible, processes found nowhere else in the dimensional scale of the Earth.

#### 5.1.1. Chemical weathering along internal mineral surfaces

We will concentrate first on internal mineral surfaces in the Earth’s near-surface environment across which primary minerals weather to secondary minerals (Banfield et al., 1991; Banfield and Barker, 1994; Hochella and Banfield, 1995; and references therein). Separating the primary and secondary phases is typically an aqueous interface where at least one of three dimensions is in the nanodomain (Fig. 2). This aqueous solution transports away ions not needed by the secondary phase, and transports in ions needed by the secondary phase. It also mediates the structural transformation of chemical components in the primary phase that will be used in the secondary phase. Yet, confined in a nanospace, this aqueous solution behaves quite differently than bulk aqueous solutions. The structure of the water in this confined space, significantly modified by the mineral surfaces on either side, results in a much lower dielectric constant (e.g., Sposito and Prost, 1982; Sposito, 1984), and a much higher viscosity than bulk water (Low, 1976, 1979; Derjaguin and Churaev, 1986). Further, in confined aqueous films, the Bronsted acidity of aqueous metals increases, i.e., coordinating water molecules are more likely to dissociate, releasing a proton to solution (Fripiat, 1976; Poin-signon et al., 1978; Sposito, 1984). Finally, as the space becomes more confined, nucleation probabilities are reduced while maximum supersaturation increases (Putnis et al., 1995, and references therein). This latter point is probably due to the difficulty of bringing growth components to the surface of a growing nucleus quickly enough for the nucleus to reach a critical (stable) size. Finally, transport in these nanospaces is most likely diffusion controlled, not flow controlled.

The upshot of the above is that, especially in the early stages of weathering, the water flowing through rocks is not representative of the water in contact with what is likely the majority of the surfaces undergoing weathering and secondary phase development (Hochella and Banfield, 1995). The water held within the internal surface areas is subject to nanodomain influences that is, as described above, dramatically different than bulk water. This is an important reason why it is difficult to compare laboratory and field-based weathering studies.

#### 5.1.2. Mineral-bacteria interaction

One of the most important interactions in the weathering environment and in soils is mineral-bacteria association. The bacteria, typically in the micron-size range, with dynamic membranes of physiologic suites of organic molecules, interact with surfaces of any one of thousands of minerals, each with their own chemistry, crystallographic orientation, and microtopography. This interaction takes place over nanometers of

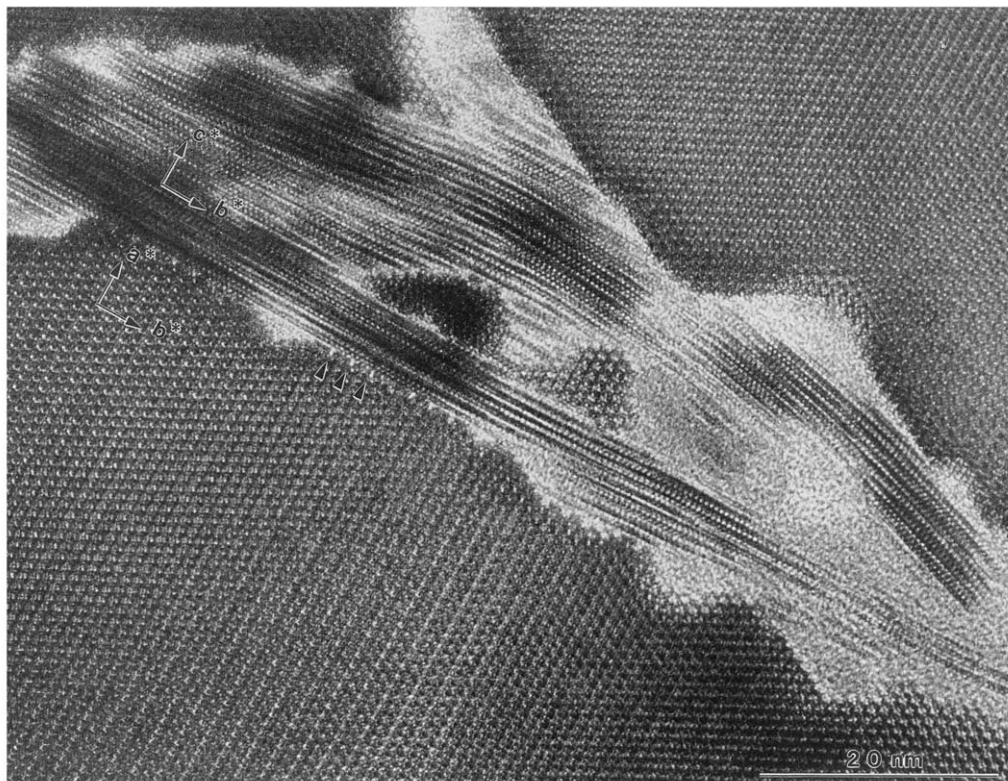


Fig. 2. High resolution transmission electron microscope image of an amphibole (large areas in upper right and lower left of image) weathering to smectite (the sheet silicate running from the upper left to lower right through the center of the image). The arrows point to subnanometer conduits between individual I-beams of the amphibole that carry aqueous fluids through which chemical components to and from the reaction front move. From Banfield and Barker, 1994.

distance as their surfaces approach one another, are in contact, and separate. Recently, all of these forces of interaction, between fully viable bacteria and various mineral surfaces in aqueous solution, have been quantitatively measured in real time using a variation of atomic force microscopy, a technique that we call biologic force microscopy, or BFM (Lower et al., 2000, 2001a, 2001b). Measurements of this type speak to the heart of nanoscience, insofar as the observer is looking at nanoNewtons of force over nanometers of distance (Fig. 3). As a bacterial cell and a mineral surface are brought closer together, the confined water layer in between is subject to the same attributes discussed just above, influencing and influenced by the macromolecular outer cell envelope of the bacterium and the mineral surface itself. Certainly, we have now been able to measure distinct and significant differences in the forces of interaction as a function of changes in the mineral surface, the intervening solution, and the bacterial surface (both in species and growth condition). It is easy to see how this aspect of nanoscience will have applications to bacterial transport and contamination in groundwater aquifers, subsurface in-situ bioremediation, the use of wastewater for irrigation or for groundwater recharge, and many other issues pertaining to mineral-microbe interaction.

## 5.2. Metal Transport Nanoscience

Metal transport in the environment is often of great environmental concern, whether related to radioactive waste disposal,

acid mine drainage, industrial pollution, or any number of other scenarios. Metal mobility ultimately depends on 1) the chemical reactivity of the metal in question as dictated by bonding characteristics and interactions; and 2) the part of the environment through which transport occurs (soil, groundwater, surface water, atmosphere, etc.). Brown (2001) and Selim and Sparks (2001) provide interesting perspectives on several aspects of these issues. A fundamental question that can be easily overlooked is simply whether the metal in question is moving as aqueous complexes, as part of a precipitate, or as sorbed complexes on particles. It is often assumed that if the metal in question passes a submicron filter (typically in the 0.2 to 0.5 micron range, i.e., 200 to 500 nm), then that metal is considered to be an aqueous species. In these cases, investigators simply have no better way to handle what is obviously missing from this approach. That is, metals can in fact, and presumably often are, transported within or on nanoparticles, not as aqueous species. In the future, as we learn to deal better with the nanoscale in terms of observation, analysis, and modeling, this assumption will be less and less necessary.

A good example of nanoparticle metal transport in the environment occurs in acid mine drainage (AMD) systems. AMD is the result of the worldwide occurrence of hundreds of thousands of working and abandoned sulfide-bearing mines and their wastes (e.g., Jambor and Blowes, 1994; Alpers and Blowes, 1994). The weathering of metal sulfide minerals in hydrated, oxygenated surface environments results in highly

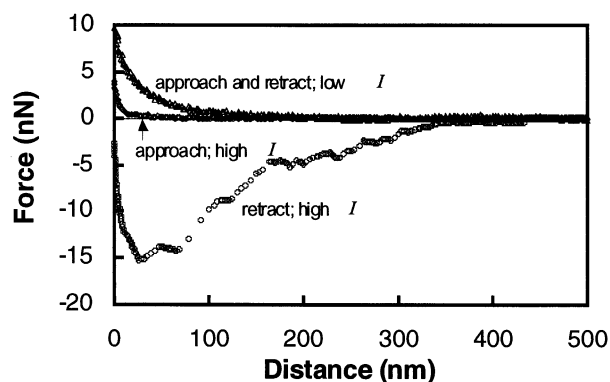


Fig. 3. Force-distance curves for *Escherichia coli* and a muscovite (001) surface in aqueous solution at pH 6, 25°C, and varying ionic strengths (high  $I = 10^{-1}$  M; low  $I = 10^{-5}$  M). On the y-axis, the sign convention is positive for repulsive forces and negative for attractive forces. The curves show that at low ionic strength, the surfaces of the bacteria and mineral repel each other. This repulsion is due to electrostatic forces (both surfaces are negatively charged at this pH) which are operative over separations of up to 100 nm. Even after bacteria-mineral contact, no adhesive forces develop between them. At high ionic strength, where the electrostatic double layers are compressed, repulsive forces are not measurable until the separation is reduced to 20 nm, and upon contact, the bacterial and mineral surfaces adhere, resulting in the retraction curve that shows up to 15 nN of attractive force. The shape of this pull-off curve is indicative of adhesion (typically measured in dimensions far greater than the nanodomain) characterized by fibrillation or stringing, the result of formation and rupture of discrete adhesive fibrils during pull-apart. In this case, the two are not completely separated until the last fibrils, presumably fully extended outer membrane components of the *Escherichia coli*, break or detached from the muscovite surface at distances approaching 400 nm. From Lower et al. (2000).

acidic effluent emanating from production and waste rock piles. At low pH's, many metals can be transported in the aqueous phase, but mine drainage waters increase in pH the further they travel from the source due to dilution by water from uncontaminated sources, as well as various buffering reactions in the streambed or aquifer. At this point, precipitating phases include iron-dominated oxides, oxyhydroxides, and/or hydroxysulfates. This results in iron-rich sediments and mineral/rock coatings that typically contain high concentrations of less abundant metals such as Cu, Pb, Zn, Cd, As, and Mn, among others. Yet, these more toxic metals can still be transported down hydrologic gradient for hundreds of kilometers, and in relatively short amounts of time, long past where iron-rich precipitates are visually apparent. The process by which this occurs has recently been directly observed by Hochella et al. (1999). Nanocrystalline Fe-oxyhydroxides can form, with the more toxic metals sorbed to their surfaces (Fig. 4a), or toxic metal-oxides can form directly in the nanometer size range (Fig. 4b). Nanosized particles can stay suspended in mine drainage waters essentially indefinitely, therefore transporting metals well down the hydrologic gradient limited only by the stability and/or coarsening kinetics of the particles. It is important to remember that the solubility of nanosized particles is greatly influenced by Eqn. 2, so that thermodynamically calculated solubilities of bulk materials may be off by orders of magnitude relative to nanoscale equivalents. Further, we are just now beginning to

learn that sorption kinetics and mechanisms of aqueous species onto nanocrystalline particles can be significantly different compared to the same sorbate attached to larger particles (Zhang et al., 1999). As more and more transmission electron microscopy is performed on AMD materials, and more sorption and solubility studies are attempted on nanoparticles known to be present in AMD environments, these systems will be much better understood and environmental assessments and predictions more robust.

## 6. THE FUTURE

The field of nanoscience is largely unexplored. Yet the results from previous research in this area are now being recognized for their importance and are forming an important foundation from which to build. Through this early work, fundamental principles are starting to take shape. However, the nanoscale is in a gray area sandwiched between quantum and classical domains. It is certain that unexpected results and their scientific consequences await us down the line.

The role of nanoscience in geochemistry, and all other fields of science for which it is relevant, has yet to be succinctly defined. Already, however, as this article has hopefully implied, we know the general directions in which nanogeochemistry is going. The first such direction is the study of nanosized particles, and this is becoming more and more sophisticated all the time (e.g., Janney et al., 2001). As stated above, nanosized particles are present in the earliest stages of crystallization in all geologic regimes, but they can persist, and are in fact very likely ubiquitous, in low-temperature earth environments. Here, the roles that they play in soil formation, mineral-microbe interactions, and environmental geochemistry, just to name a few areas, are poorly understood. Because surface energies can effectively dictate the formation of a particular polymorph of any given composition in the nanodomain (e.g., McHale et al., 1997), such polymorphs will have to be identified and their properties characterized in this size range. Geochemically important characteristics such as stability ranges, solubilities, sorption behaviors, and reaction kinetics will need to be specifically measured for these nanosized particles. Large differences relative to the same phase, but coarser, should be expected.

A second major research direction in nanogeochemistry will be the study of nanothin films. Like the alumina coating on the aluminum wire in the example given earlier, films with nanometer thickness can have surprising properties. In many cases, simply determining that such a nanofilm exists on a mineral surface or between minerals can be a difficult proposition requiring sophisticated techniques (e.g., Tingle et al., 1990). But doing so may be the key to many studies because these films can mask the underlying mineral and provide their own unique surface reactivity. Nanofilms can even play a role in geophysical studies of the Earth. Carbonaceous films discovered in many mid to deep crustal rocks (Tingle et al., 1991; Mogk and Mathez, 2000; and references therein) are most likely responsible for the relatively high electrical conductivity of rocks from this part of the Earth.

Finally, a third major research direction in nanogeochemistry will be the study of nanosized features and processes on surfaces (Scheidegger and Sparks, 1996, provide an excellent early review of this subject). Chemists and chemical engineers have designed many successful heterogeneous catalysis sys-

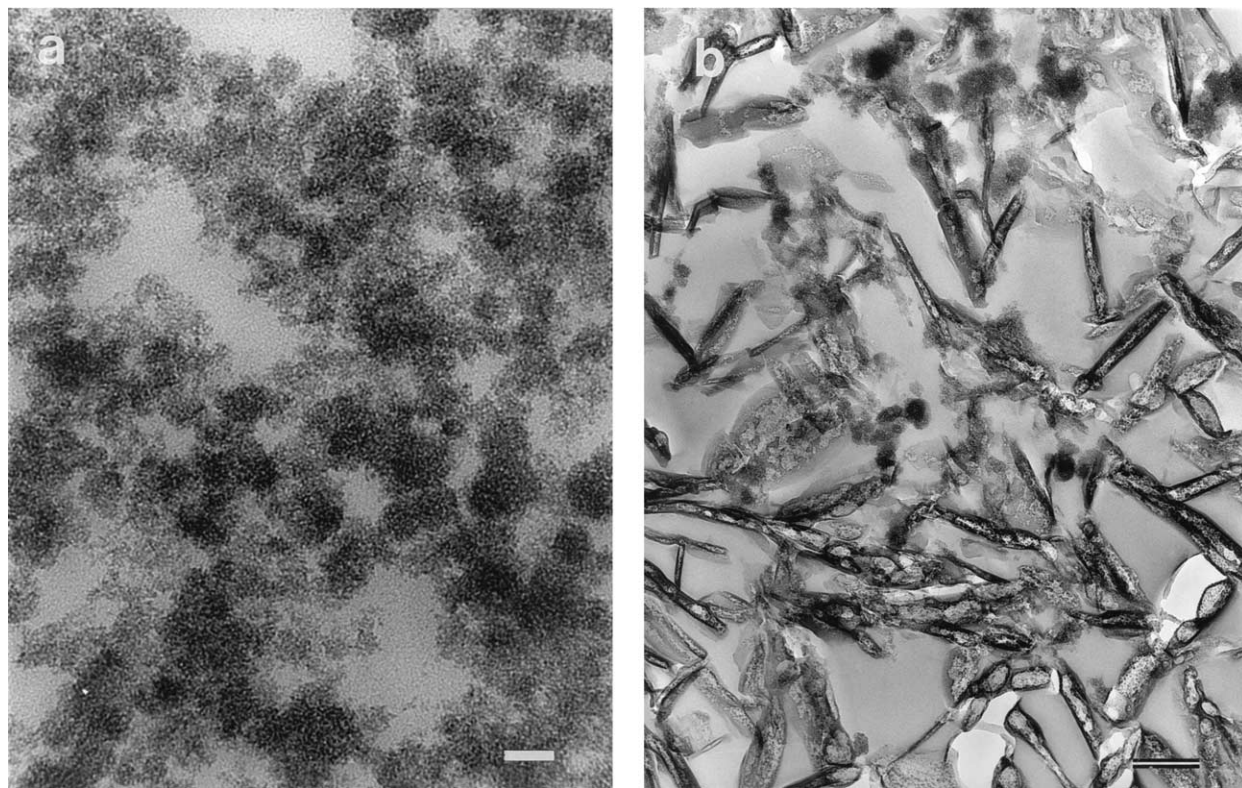


Fig. 4. (a) Bright field TEM image of ferrihydrite aggregates in bed sediments from a channel carrying drainage waters emanating directly from the main adit of the Mike Horse Mine located within the Heddeleston District of west-central Montana, USA. Mineralized veins in this mine consist principally of quartz, pyrite, galena, sphalerite, and chalcopyrite. Electron diffraction clearly shows the ferrihydrite (nominally  $5\text{Fe}_2\text{O}_3 \cdot 9\text{H}_2\text{O}$ ) to be of the “two-line” type, that is the more amorphous variety of this mineral. Aggregates in this image are on the order of 50 nm in diameter, but these aggregates are clearly made up of much smaller, nanometer-sized crystallites. TEM/EDX and EFTEM/EELS spectra show these aggregates to be composed principally of Fe and O, as expected, but they also have significant concentrations of Zn, Cu, Si, and Al, elements that are inferred to be sorbed to the ferrihydrite surfaces due to the lack of evidence of any other phase in this material. Scale bar = 50 nm. See Hochella et al. (1999) for details. (b) Bright field TEM image of gahnite ( $\text{ZnAl}_2\text{O}_4$ ) rod-shaped aggregates from the same location described in (a). Electron diffraction patterns from these aggregates (Hochella et al., 1999) show that they are made up of distinct single crystals, and visual inspection of this and other images indicate that these crystals are in the size range of roughly 5 to 10 nm. TEM/EDX and EFTEM/EELS spectra show the presence of only Zn, Al, and O as expected for gahnite, with no significant amounts of other elements sorbed to the gahnite surfaces. Scale bar = 200 nm.

tems, some of which should have natural analogs. We need to look for these analogs and determine their role in geochemical processes. Related to this is the recent discovery of the surface proximity effect (Becker et al., 2001) in which a chemical reaction at one surface site influences the electronic structure and reactivity of neighboring and nearby sites usually within nanometer distances. Clearly this influences the overall surface reaction mechanism, and models like surface complexation theory will have to be modified to take these newly discovered nanoscale phenomena into account.

One might think of nanoscience as the last frontier of materials science, clearly developing well after research on either side of the nanoportion of the dimensional scale. To me, this is the observation and realization that assures the one thing certain about nanoscience, and that is that it will make an important and lasting difference to fields that it clearly impacts. Insofar as geochemistry is one of these fields, we have quite a revolution to look forward to.

#### NOTE ADDED IN PROOF

Banfield and Navrotsky (2001) was published after this article was written. It is an important source of information on nanoscale particles in the environment.

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