

Frontiers

Nanoscience and technology: the next revolution in the Earth sciences

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Abstract

Nanoscience and technology are not exactly new, but nevertheless rapidly expanding fields that are providing revolutions in all sciences on the scale of what genomics and proteomics have done in recent years for the biological sciences. Nanoscience is based on the fact that properties of materials change as a function of the physical dimension of that material, and nanotechnology takes advantage of this by applying selected property modifications of this nature to some beneficial endeavor. The prefix ‘nano’ is used because the property dependence on physical size is generally observed close to the nanoscale, somewhere around 10^{-9} m. The dimensions at which changes are observed depend on the specific material and the property in question, as well as which of the three dimensions are restricted in real space (e.g. small particles vs. thin films vs. ‘one-dimensional’ phases). Properties change in these confined spaces because the electronic structure (i.e. the distribution of electron energies) of the material is modified here in the gray area between the bulk and atomistic/molecular realms, or equivalently between the continuum and strictly quantum domains. Earth materials with at least one dimension in the nanorange are essentially ubiquitous. Many have been known for several decades and more are being discovered all the time. But the scientific emphasis has now shifted to that of measuring, understanding and ultimately predicting the property changes from the bulk to nanodomains, and to the understanding of the significant ways that Earth processes are affected by these changes. In addition, where possible, Earth scientists are using nanoscience to develop nanotechnology that should play important roles in Earth sustainability issues of the future.

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1. Introduction

See if you can answer this question. What do the following three technologies have to do with

each other or, for that matter, with the Earth sciences?

- Antiferromagnetically coupled (AFC) media. By this year, computer hard disk drives were quickly approaching the theoretical limit in data density for the existing technology of magnetic storage (20–40 gigabytes (GB) per square inch). But with the use of AFC, the first major change in hard disk media materials and design

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in some time, data densities of four times that, and beyond, are obtainable. In AFC recording media, a layer of ruthenium three atoms thick is sandwiched between two much thicker magnetic layers. This allows stable magnetic domains in the layers above and below the ruthenium to be much smaller than previously obtainable while remaining stable over time. This technology will allow 400 GB desktop drives (equivalent to the data on 80 DVDs or 600 CDs), 200 GB drives in notebook computers, and 6 GB drives in handheld devices, all within two years.

- High density xerogel-based sensors. Xerogels are hard but highly porous glasses made by sol-gel processing techniques. The pores are extremely small and one can stabilize and trap proteins within these pores. The sol-gel solutions that will generate the xerogels containing various proteins are then ‘pin-printed’ on LED (light emitting diode) surfaces. Pin-printing allows for the deposition of very small quantities of activated xerogels to be placed on an LED surface at high densities. The stabilized proteins on the LED display can then be used to detect hundreds of chemicals simultaneously.
- The Lycurgus Cup. This is a wonderful example of a rare type of intricately ornamented glass cup of Roman origin. This particular object dates to the fourth century AD and displays the myth of King Lycurgus. In this silica-based glass, exceptionally small crystallites of gold are dispersed throughout. When the cup is viewed in reflected light, it appears yellowish-green in color. When viewed with light coming through the glass (transmitted light), it appears ruby-red. After Roman times, the art of making this beautiful and highly prized glass was lost and not rediscovered until the 17th century.

Here now is the answer to the first part of the question that began this article. The common denominator of these three seemingly disparate topics is nanoscience and technology. More specifically, in each case above, the surprising properties of the materials described are dependent upon the physical dimension of at least one phase. In

the Roman glass, the gold crystallites impart the unexpected coloration properties and these are limited in size in all three dimensions. For xerogels, the proteins are limited in two dimensions in the glass pores. Finally, for AFC materials, the ruthenium is limited in one dimension, and extensive in the other two. As we shall see in Section 2 of this article, it is these dimensional limitations, typically near the nanometer scale ($1 \text{ nm} = 10^{-9} \text{ m}$ or 10 \AA), that are causing these materials to exhibit unexpected properties, that is, properties that we are not familiar with in the macroscale. The understanding and explanation of these effects are the basis of nanoscience and their implementation is the basis for nanotechnology.

What is the answer to the second part of the opening question, that is, what does this have to do with Earth (and planetary) science? The examples above are all indirectly related to the geosciences because the same phenomena that allow for these surprising properties are active in a wide variety of Earth materials with nanometer size limitations in at least one of three dimensions. As described in Section 4, it is becoming more and more apparent that such materials are ubiquitous in the hydrosphere, atmosphere, and solid Earth. It appears highly likely that these nanomaterials significantly affect the nature of this planet, but we have yet to discover the details, critical explanations, and overall consequences. Actually, a smattering of such research, cloaked in different terminology compared with that used today, appeared as early as several decades ago, although scientific historians suggest that nanoscience was not clearly defined until 1959 by American physicist Richard Feynman. Nanoscience research in the geosciences has seen a significant increase especially in the last 10 years [1], and very recently it is starting to see an exponential growth due to nanoscience advances in other fields and a large influx in funding (see Section 6).

The aim of this article is to succinctly define and describe the fundamental basis of nanoscience (this follows in the next two sections), and then to explain and demonstrate why this field will play what must be described as a revolutionary role in the Earth sciences of the future.

Table 1
Simple relationships that form the basis for various fields of science

Field	Relationship	Description
Newtonian physics	$F = ma$	classical mechanics
Matter/wave duality	$\lambda = h/(mv)$	de Broglie relationship
Diffraction physics	$n\lambda = 2d\sin\theta$	Bragg's law
Quantum mechanics	$\hat{H}\Psi = E\Psi$	Schrödinger equation
Nanoscience	$P_{i,q} = f(l_x, l_y, l_z)$	property i of material q is a function of three dimensions

2. The remarkable importance of physical size

There are certain fundamental and surprisingly succinct mathematical statements that provide the foundation of various fields of science, a few of which are listed in Table 1. Despite their simplicity, they put powerful imprints on complex and extensive fields. Although such a precise, quantitative statement cannot be written yet for nanoscience in a strict mathematical sense, it is possible to express it as a functionality (Table 1) and in words as follows: any property of any material may change, even dramatically, as a function of the physical dimensions of that material. Put more succinctly: material properties change with size. Just like the other relationships listed in Table 1, such a statement is definitely not intuitively obvious to the casual scientific observer except perhaps in hindsight. Yet in this simple statement, we find the essence of nanoscience and the foundation of nanotechnology. This is because these changes in properties with material dimension are typically not observed until at least one dimension of the material is reduced down into the nanodomain. In fact, this nanodomain or nanoscale is often defined by the bit of dimensional space [1] where these property changes are observed, and that is typically in the 1–100 nm domain. All this is complicated by the fact that the dimension(s) at which a property will start to be modified depends on the material (e.g. whether a metal, semiconductor, or insulator) and the specific property in question (electrical, optical, mechanical, structural, or thermodynamic). A general explanation of this behavior is given in Section 3.

Although nanoscience is clearly in its infancy in the Earth sciences and all other sciences, it is not exactly new. As described in Section 1, fourth century Roman glassmakers unknowingly utilized

nanodomain property change phenomena in the production of glasses that contained nanoscale gold crystals. In modern science, chemists have known for several decades that very small crystals (in the nanodomain) seem to be more soluble than macroscopic crystals of the same phase. This was applied to mineral dissolution as early as 1961 [2]. This solubility dependence on size has been formulated in a modified version of the Kelvin equation as follows (e.g. [3]):

$$\frac{S}{S_0} = \exp\left[\frac{2\gamma\bar{V}}{RT\bar{r}}\right] \quad (1)$$

where S is the solubility (in mol/kg H₂O) of grains with inscribed radius r in m, S_0 is the solubility of the bulk material, γ is the surface free energy in mJ/m², \bar{V} is the molar volume in m³/mol, R is the gas constant in mJ/mol·K, and T is the temperature in K. The equation describes the observation that as the grain dimensions decrease, the solubility of that grain will go up exponentially relative to the measured solubility of a macroscopic grain where its size has no appreciable effect on solubility. If one takes into account the surface free energy estimates of oxides and silicates and their molar volumes, the measured solubility only deviates from the macroscopic value as the radius of the particles being dissolved gets very small, that is, down to the nanoscale. For example, Fig. 1 shows a plot of Eq. 1 (i.e. S/S_0 vs. r) for quartz. The solubility of small grains of quartz, according to this equation, does not begin to deviate significantly from bulk solubility until the grain size goes below 10 nm. At 1 nm, the solubility is predicted to increase dramatically.

Examples of the nanoscience principle are finally becoming more abundant in the literature in just the past few years, but this is still, quite

Table 2

Extremes in the physical properties of β -CdS (hawleyite) as a function of particle size, from the macroscale to the smallest crystals

Physical property	Macroscale β -CdS	Nanoscale β -CdS	Reference
Band gap	2.5 eV	4.5 eV	[5]
Radiative lifetime	nanoseconds	picoseconds	[5]
Melting temperature	1600°C	400°C	[6]
Transformation P	2 GPa	9 GPa	[7]

literally, only the very beginning. One of the best examples to date is actually from a mineral phase recently studied by nanoscale experts in the fields of chemistry and physics due to the tremendous potential applicability of quantum dots to science and technology. (Quantum dots are nanocrystals that, when stimulated, emit monochromatic radiation, the exact wavelength of which is a function of the crystal size.) The material is the cubic cadmium sulfide β -CdS (mineral name: hawleyite), which is isostructural with the common mineral sphalerite (ZnS). As can be seen in Table 2, physical properties of β -CdS can be dramatically altered simply by considering a particle in the nano-

scale size regime vs. a macroscopic particle. While moving from particle sizes in the macroscale down to the nanoscale, the material goes from a wide band gap semiconductor to an insulator and the radiative lifetime for the lowest allowed optical excitation decreases by nearly three orders of magnitude. In addition, the melting temperature decreases four-fold, and pressure at which Cd and S coordination changes from tetrahedral to octahedral increases by over four times.

Another mineral phase that all geoscientists are familiar with, and one for which intriguing (although limited) nanoscience information is presently available, is gold. The well-known and industrially important melting point of gold is 1064°C. However, for gold grains 4 nm in diameter, the melting point has been measured at only 427°C [8]. Gold has also been known since antiquity as an inert metal and this, combined with its rarity and beauty, have made it invaluable through history for monetary and ornamental uses, and, in addition, in modern times for electronics, optical surfaces, and so on. However, again, when reduced in size into the smallest portion of the nanodomain, gold is anything but inert. In the extreme, gold atoms are powerful reductants and are instantly oxidized in air [9].

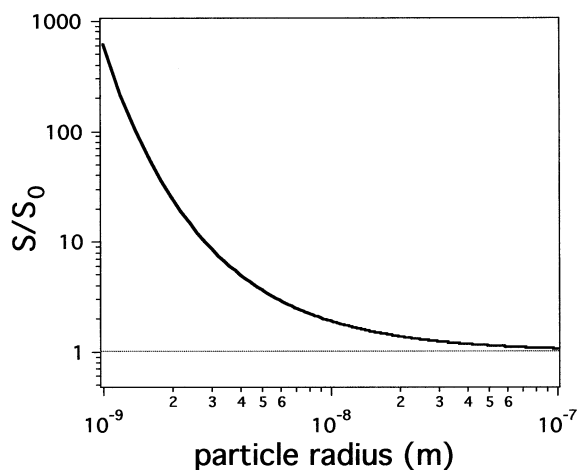


Fig. 1. The deviation of the solubility of small grains of quartz relative to its bulk solubility (S/S_0) as a function of the size of the quartz grains being dissolved according to Eq. 1. The following values were used to produce this curve: $T=298$ K, $\bar{V}=22.68 \times 10^{-6}$ m³/mol, $\gamma=350$ mJ/m² (from the compilation of surface free energies for quartz [4]). At a particle radius of 10^{-7} m (100 nm), the solubility is indistinguishable from the bulk value. By the time the particle radius is reduced to 10^{-9} m (1 nm), the predicted solubility is nearly three orders of magnitude higher.

3. Comments on property–size dependence based on electronic structure

The emergence of nanoscience of the last two decades has resulted in rationalizations, and in some cases explanations, of the physical property dependence on material dimension. At first glance, one might expect to rationalize property modifications as the material dimensions are reduced using atomic structure modifications. This

might be especially true for surface structure because, as the size of a particle decreases, the fraction of atoms on and near the surface goes up exponentially. Also, surface energy is critical in explaining the relative thermodynamic stability of nanocrystalline polymorphs (e.g. [10]). In fact, structural modifications within and on the surface of nanoparticles have been documented relative to the equivalent in/on macroscopic samples [11]. However, insofar as all physical properties are ultimately dependent on the electronic structure (i.e. the energy distribution of electrons) of the material, we concentrate on this aspect next.

For molecular orbitals in molecules, the outermost (valence) electronic levels on constituent atoms mix, changing in energy, to create bonding, non-bonding, and anti-bonding orbitals. If these molecules are joined to make an extended structure, that is, a macrosized object, the well-defined energy levels just referred to are smeared into bands which cover a range of energies. However, these bands are still well defined. All electrons in the extended phase must be accounted for in these bands, and the greater the overlap of orbitals on neighboring atoms or molecules, as, for example, for the orbitals involving valence electrons, the greater the energy spread of the band, or, equivalently, the wider the band.

If we consider the distribution of electronic states within one band (say the valence band) of a material as a function of dimension, we see a continuous distribution of electron energy states in that band in the macroscopic material (Fig. 2). As the dimensions of the material are reduced, the distribution of states starts to become discontinuous working from the edge towards the middle of the band. By the time the particle is reduced to a single representative molecule, the states in the band are all discontinuous, with electrons only occupying discrete, clearly separated states. In the valence band, each of these energy states represents a bonding or non-bonding orbital for that molecule. Clearly the physical properties of the material will be affected, and dramatically so, by this alteration. The specifics of this dependence are a complex and extensive subject, especially in this dimensional range. A quantitative understanding of this, much of which will come from

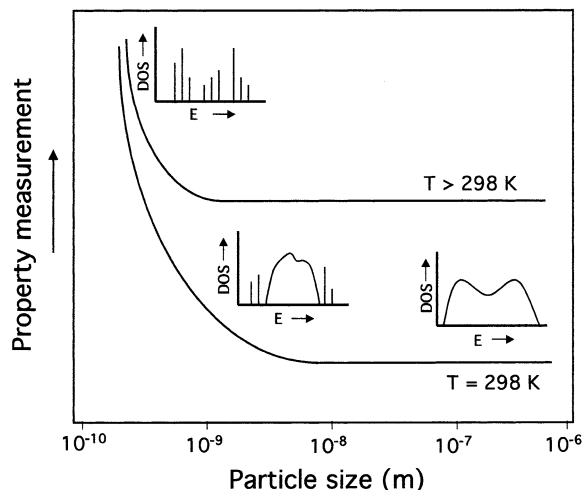


Fig. 2. Schematic drawings of the electron distribution of a valence band of a material as a function of size for room temperature and an arbitrary higher temperature, along with some physical property measurement over this same size regime. Each plot shows the energy (E) of electronic states within that band vs. the density of states (DOS). The higher the DOS, the more densely packed the electronic states that occupy that near-region of energy ($E+dE$). Therefore, in filled states like in the valence band, DOS curves plot or display the distribution of electrons as a function of energy for that material. Note that, at the higher temperature, the physical property begins to change at a smaller particle size. This is because the higher temperature will allow the separated states on the edges of the bands to ‘communicate’ a bit longer due to thermal smearing (Eq. 2).

theoretical modeling, is a great challenge for the future [12].

It is prudent to raise one final point in this section. The nature of the ‘connectedness’ of states, as they become more discontinuous with reduced size, also depends on temperature. Using standard statistical mechanics, the Maxwell–Boltzmann energy distribution of particles (in our case electrons) about an energy state E , that is, $n(E)$, is given by:

$$n(E) = K \exp(-E/2k_B T) \quad (2)$$

where the constant $K = n(m/(2\pi k_B T))^{3/2}$ and n is the average number of electrons per state, m is the electron mass, k_B is the Boltzmann constant, and T is the absolute temperature. This relationship predicts that, as the temperature increases, the

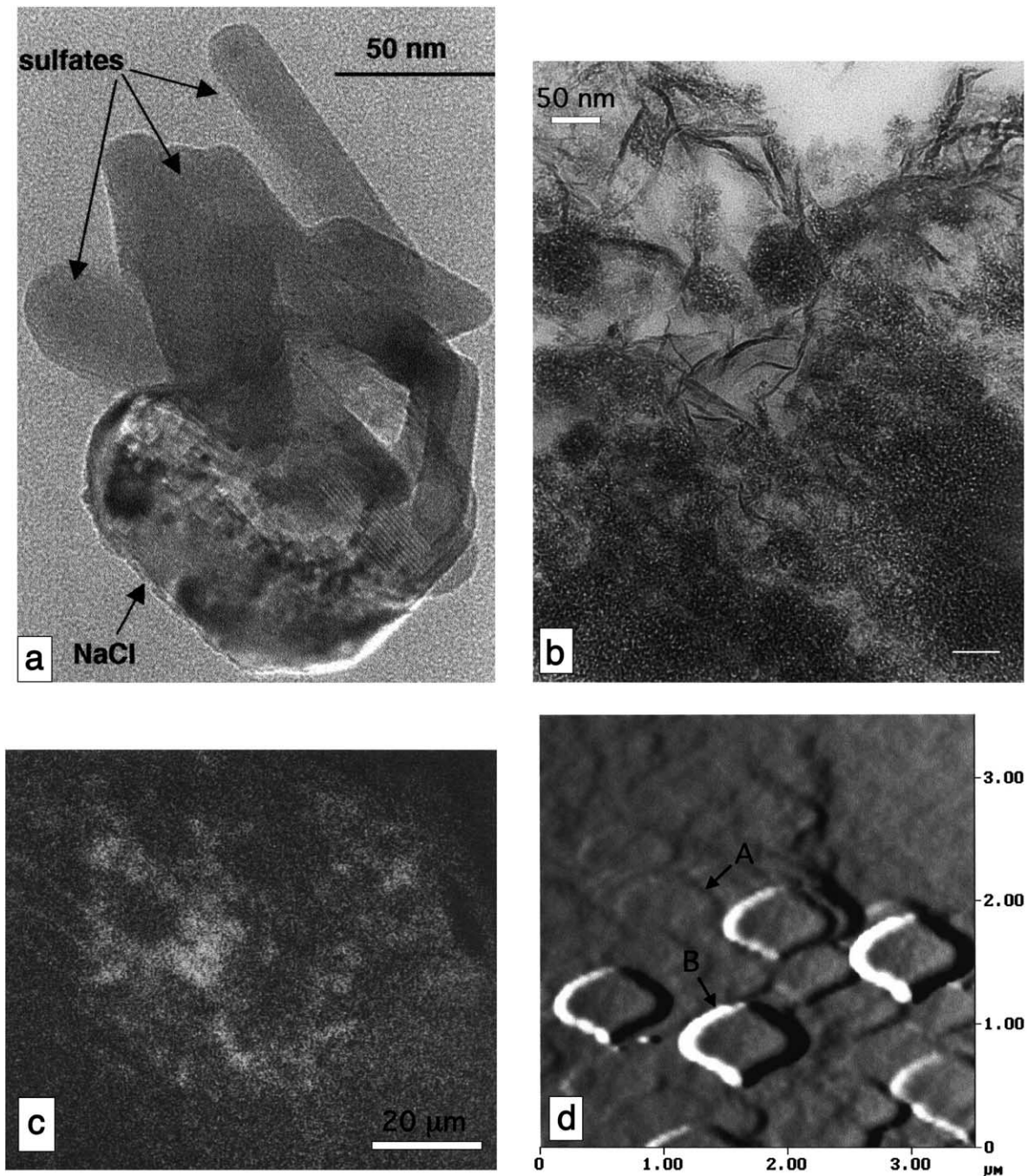
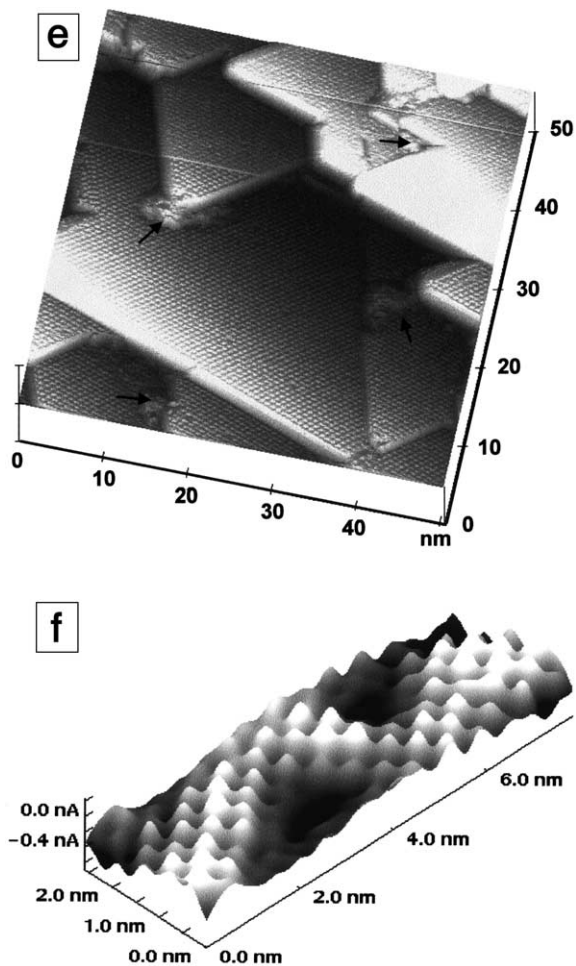


Fig. 3.

electron energy distribution $n(E)$ about some electron energy state E increases, and by how much. Now we can add to the description above that when the energy spacings of electrons at a given

temperature exceed the energy distribution due to the smearing effects of that temperature as described in the Maxwell–Boltzmann distribution, properties will change. The lower the temperature



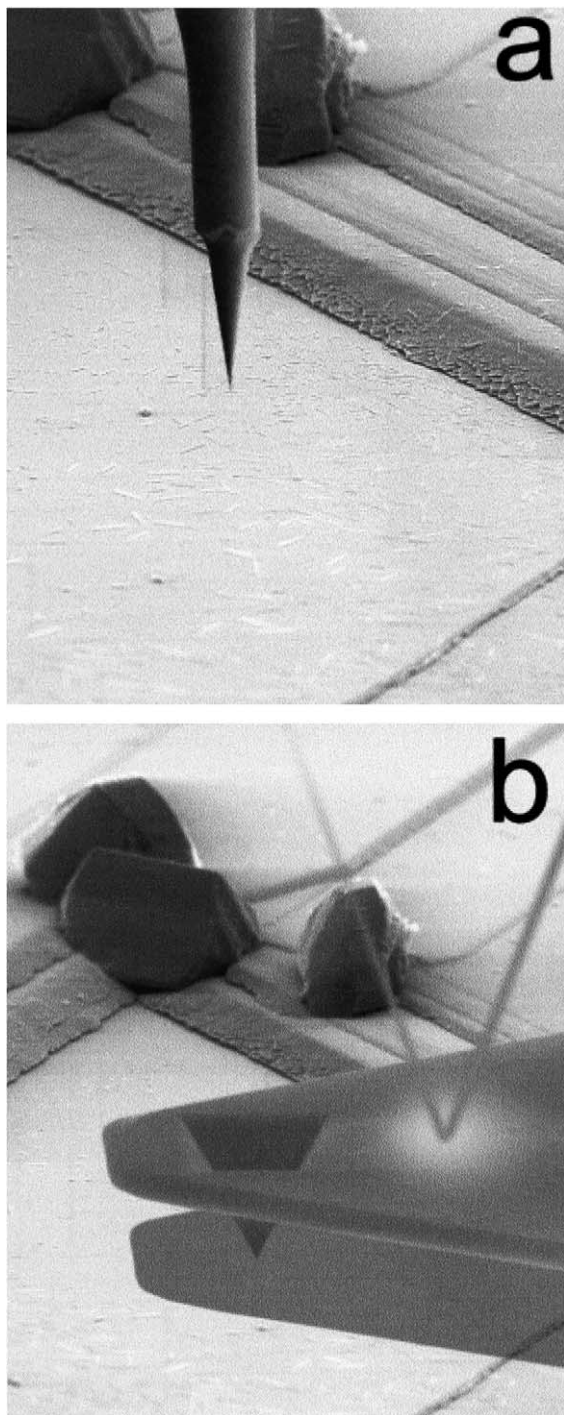
(for example Earth surface temperatures vs. hydrothermal temperatures), the earlier the material will start to exhibit property changes as it is reduced in size (Fig. 2). Equivalently, for a particle growing from the nanodomain, that particle will retain non-bulk properties longer growing at lower temperatures than if it is growing at higher temperatures.

4. Nanoscience and understanding the Earth and planets

Where in the Earth system (and for that matter in any planetary system) does one find materials with at least one of their dimensions limited to the

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Fig. 3. A sampling of nanomaterials, three (a–c) taken directly from nature and three (d–f) taken from laboratory experiments designed to capture what is likely present yet transitory in Earth surface environments. (a) TEM image of an atmospheric sea-salt aerosol particle consisting of several grains in the nanodomain (from Buseck and Pósfai [13]; image taken by M. Pósfai). These aerosols are important in solar radiation scattering, as cloud condensation nuclei, and in the cycling of atmospheric Cl, S and N through gas/aerosol surface reactions. This particle was collected in the troposphere over the Southern Ocean near Tasmania. (b) TEM image of ferrihydrite (the stippled portion of the image, mostly in the lower half) and hydrohetaerolite (the fibrous phase, mostly in the upper half) (image collected by M. Hochella). The ferrihydrite (an iron oxyhydroxide) consists of nanometer-sized semicrystalline particles, and the hydrohetaerolite, a Zn, Mn oxide hydrate, is a ‘one-dimensional’ phase, with fibers as narrow as 1 nm. These phases are from an acid mine drainage site in Montana, USA, and are important in the transport of toxic metals into the environment [14]. Scale bar = 50 nm. (c) Carbon X-ray map (collected with an EDX detector in an SEM with white dots indicating a carbon signal) of a crack surface from the interior of a large olivine single crystal ([15]; image collected by T. Tingle). The crystal is from a xenolith hosted in an alkali basalt from San Carlos, AZ, USA. The carbon film is essentially continuous over this surface, but thickens in places, as shown by the concentration of white dots. This carbon film contains abiotic organic molecules with thermally emitted fragments in excess of 200 amu. Sputter depth profiling using Ar ion bombardment and X-ray photoelectron spectroscopy shows the film to be generally less than a few nm thick. Scale bar = 20 μm . (d) AFM image of ‘two-dimensional’ crystals of schoepite (a uranium oxyhydroxide hydrate) growing on a calcite surface in an aqueous metal–mineral partitioning experiment [16]; image collected by M. Schindler). The diamond-shaped schoepite crystals in this image are 1000 nm long, but only between 3 and 7 nm thick, corresponding to between 2 and 4–5 unit cells (arrow A points to a crystal 2 unit cells thick, arrow B to a crystal 4–5 unit cells thick). X – Y scales are in μm . (e) STM image of a 50×50 nm area of a pyrrhotite (Fe_7S_8) surface in vacuum after exposure to oxygen [17]; image collected by U. Becker). The small white dots on the flat terraces represent individual surface sulfur atoms. The steps between terraces are 0.3–1.7 nm in height in this image. Arrows point to nanometer-sized oxidation products that usually form from step bases where the steps change directions, but never starting out on the terraces themselves. X – Y scales are in nm. (f) STM image of a pyrite (FeS_2) surface in vacuum [18]; image collected by K. Rosso). The bumps represent individual iron atoms on the surface. The sulfur dimers in between are not visible under these tunneling conditions. The dark areas are 1–2 nm-sized surface oxidation patches after exposure in the vacuum to minute amounts of oxygen. X – Y scales are in nm.



nanoscale? The answer is simple, yet rather daunting. As best we can tell, they are literally everywhere. If you have the tools to look (see [Section 5](#)), you will find them throughout all soils and in all parts of the solid Earth to which we have access (and presumably most parts that we do not), at every level of the atmosphere, and throughout the hydrosphere. Such should be the case for the solid components and the hydrosphere/atmosphere (if applicable) of any planet. We know that, on this planet, both organic and inorganic nanomaterials are related to pure geosystems as well as biogeosystems. These nanomaterials include, but are not limited to, nanoparticles (e.g. [Fig. 3a,b](#)), thin films (e.g. [Fig. 3c](#)), ‘two-dimensional’ crystals (e.g. [Fig. 3d](#)), and ‘one-dimensional’ materials (e.g. [Fig. 3b](#)). One also needs to include nanoscale domains and features within and on macroscale materials (e.g. [Fig. 3e,f](#)). The lifetimes of nanomaterials vary tremendously, from essentially instantaneous in, for example, the crystal nucleation and growth process under supersaturated conditions, to longer

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Fig. 4. (a) The tip and sample in a typical STM experiment. The tip is a pointed metal probe attached to a ceramic piezoelectric scanner. By applying voltage to the scanner, the ceramic distorts, resulting in subtle movements of the tip, controllable to within 0.1 \AA in x , y and z . At very small separations ($<1 \text{ nm}$) and with the application of a small bias voltage (usually in the mV range) between the tip and a conducting or semiconducting sample, a minute tunneling current (usually in the nA range) can be detected between the two. This current, resulting from overlapping orbitals for atoms at the end of the tip and on the surface of the sample Angstroms away, is extremely localized and can change, for example, by an order of magnitude over a 1 \AA distance. This is what gives STM atomic resolution in imaging and spectroscopy. (b) The imaging of a mineral surface by AFM. The sample (not the probe as in STM) is usually placed on a piezoelectric scanner (see (a) for scanner description). The probe typically consists of a very sharp tip on the end of a thin silicon nitride microcantilever. A laser, reflecting off the back of the microcantilever, is directed into a photodiode sensor (not shown). The optical ‘lever arm’ is such that deflection of the cantilever in the 1 \AA range is detectable. AFM imaging is typically accomplished by rastering the sample in x , y and z so that the microcantilever stays stationary. A vertical resolution and nm lateral resolution is typical, although \AA lateral resolution is possible.

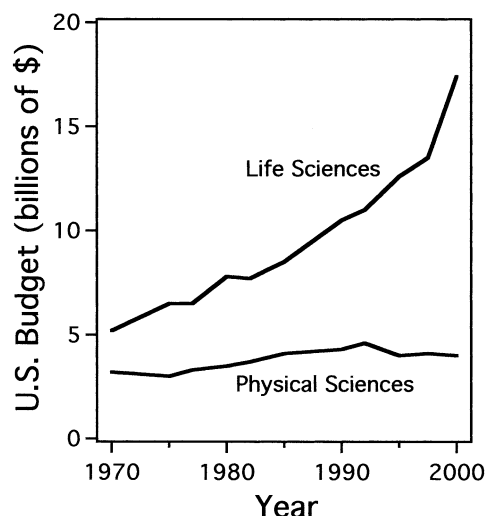


Fig. 5. Federal funding of science in the United States from 1970 to 2000 according to the National Science Foundation. Data are plotted in terms of inflation-adjusted (constant) dollars. Funding for the physical sciences has remained essentially flat over this time period, while funding for the life sciences (mostly health-related sciences) has more than tripled over the same span of years. Large influxes in funding for nanoscience within the physical sciences are likely to modify these diverging trends in the near to longer terms.

term, for example, ultra-fine mineral dust in the atmosphere.

The next logical question is, how will observing and understanding these nanocomponents and their properties significantly affect our understanding of the workings of this planet? Below is a sampling of specific examples where nanoscience has already impacted the geological sciences just in the last few years, each given with a representative reference:

- minerals in the troposphere, including nanominerals, with implications for radiative forcing effects and consequently global heating/cooling [19];
- the general formation, growth, and nature of airborne nanoparticles, with implications for human health effects and atmospheric chemistry, including heterogeneous catalysis on nano-aerosols [20];
- carbonaceous nanofilms in many crystalline rocks of deep crustal and mantle origin, with implications for the relatively high electrical conductivity of these rocks [21];

- organic nanofilms in volcanic rocks, with implications for complex abiotic heterogeneous catalysis and synthesis [15,22,23];
- mineral nucleation and growth in the nanodomain, with implications related to the initial growth of minerals [24];
- heterogeneous nanoprecipitation at the mineral/water interface in soils, with implications for the transport and distribution of toxic metals in the environment (e.g. [25]);
- mineral surface reactivity in the presence of nanofilms of water, with implications to weathering reactions and the formation of secondary phases [26];
- the complexation of aqueous solution components in polynuclear complexes and nanoclusters, with fundamental applications in the areas of aqueous geochemistry and biogeochemistry [27];
- metal sorption on nanominerals in acid mine drainage environments, with implications to toxic metal transport in surface and groundwater systems [14];
- the characteristics of naturally occurring magnetic nanoparticles, with implications for biological systems, remediation strategies, medicine, and so on [28,29];
- nanomolecular attachments between minerals and microbes, with implications for bacterial attachment and electron transport between living and non-living systems [30].

This list is intended to be illustrative, and is by no means exhaustive. There are many other examples already in the literature. But just from the list presented here, one can project that nanoscience will one day account for significant portions of research in the subfields of mineralogy, petrology, geochemistry and biogeochemistry, atmospheric science, hydrogeoscience, geophysics, and perhaps other subdisciplines.

How else might nanoscience and technology of the future affect the Earth and planetary sciences? The answer in this case is an indirect one, yet perhaps no less important. The promise of the future of nanotechnology, in fact the very reason for massive investment in this field already in both public and private sectors, is an array of new devices and tools. At the forefront of the nano-

technology parade are the beginnings of computers that will not be based on the silicon chip technology of today and their fast approaching limitations. These are computing machines based on molecular scale transistors and semiconducting nanowires [31]. Such computers, built from the bottom up with nanotechnology instead of from the top down using silicon wafer manipulation, will result in computational resources many orders of magnitude beyond current technologies. Clearly, such computing power will impact Earth and planetary modeling. In addition, new ways to detect and sense everything from chemistry to physical conditions are being developed using nanotechnology (see Section 1 for an example). These will revolutionize not only how we detect various aspects of the Earth and planets, but what we detect. Advances in both these realms (computing and detection/sensing) will change our science.

5. Tools of the trade

In order to study the physical and chemical processes occurring in the nanoscale, one must have tools that can see (i.e. microscopy), interrogate (i.e. spectroscopy), and predict (i.e. models) what happens there. Forms of this triad have been available for decades. But the situation unexpectedly and dramatically improved in 1982, and we are currently in the midst of an explosion of nano-capable tool development. Here is the story from the beginning in brief.

The father–son team of W.L. and W.H. Bragg first successfully determined the atomic arrangements in solids, starting in 1912 using X-ray diffraction techniques, and these are still important in nanoscience today [11]. In the 1930s, Max Knoll and Ernst Ruska made breakthroughs in electron optics that immediately led to the development of the first microscopes based on electron beams. From this, the transmission electron microscope (TEM) was born, and after a history of improvement and refinement that has lasted decades, TEMs are one of the most important tools in nanoscience today. In a single instrument, one has the ability to study the morphology,

atomic structure, and composition of mineral nanoparticles and nanofilms [32]. Another tool, extraordinarily versatile because it is element-specific and its application is independent of sample state, is X-ray absorption spectroscopy (XAS). Primarily a synchrotron-based technique, it can be used to probe the local atomic structure of targeted elements, including those in or on nanoparticles and films (e.g. [33]).

One of the most important instrumental breakthroughs in the 20th century, and the most important development in nanoscience and technology instrumentation ever, was the unexpected and surprising invention of the scanning tunneling microscope (STM) in 1982 [34]. The great physicist Erwin Schrödinger, who played such a key role in forming the foundation of computational quantum mechanics that we use today, predicted in 1952 that we would never experiment with just one atom or molecule. The STM changed all that very quickly. Along with its first principal offspring developed shortly thereafter, the atomic force microscope (AFM, also known as the scanning force microscope or SFM; see [35]), such feats are not only possible, but relatively ‘routine’. The electronic signatures of individual atoms can be investigated using STM and scanning tunneling spectroscopy (STS) on conductors and semiconductors, the latter of which include many important minerals (Fig. 4a). STM and STS can give unprecedented insight into how and why atoms behave the way they do in the nanoscale [18]. But the majority of minerals are insulators and here the AFM has become the scanning probe microscope (SPM) of choice. Although chemical information is not obtainable directly with AFM, nanoscale topography of surfaces, in real time and in situ (e.g. in aqueous solution), can be easily obtained (Fig. 4b). AFMs have allowed for considerable advances in mineral growth and dissolution studies.

Other more highly specialized SPMs have been designed to take specific advantage of optical properties (scanning near-field optical microscope, or SNOM), electrochemical reactions (scanning electrochemical microscope, or SECM), magnetic properties (magnetic force and resonance microscope, or MFM), and thermal properties (scan-

ning thermal microscope, SThM) [36]. SPMs have even been designed to follow individual atoms as they diffuse across a surface [37]. A detailed text on all aspects of the STM and AFM, along with many other related SPM techniques, can be found in [38].

Although STM, AFM, TEM, and X-ray-based techniques provide a powerful combination of methods to observe and characterize nanoscale materials and processes, there is still a great need for additional tools with even greater versatility. Instrumental physicists are continually refining established techniques and inventing new ones that will become important in nanomaterial characterization. Some of these developments may not be particularly useful to Earth scientists. But some, with time, will prove to be indispensable. Tools that would fit this latter category are additional three-dimensional microscopy systems capable of nanoscale resolution. Such systems may eventually be based on non-linear (multi-photon) optical microscopy, as well as ultrasonic and thermal imaging.

With ultra-high brilliance, third generation synchrotron X-ray sources coming on line, as well as advances in X-ray focusing optics, rapid analysis of nanosize particles is within reach (e.g. [39]). And it is also likely that SPMs of the future will be simultaneously multi-functional, giving a wide range of characterization in very short times.

Finally, indirect tools, such as wet chemistry experiments to measure sorption characteristics of nanoparticles in solution [40], will of course continue to be absolutely invaluable and in the mainstream of nanogeoscience research.

6. Funding, and more funding

Few would argue that government funding increases in the medical sciences are inappropriate. What many believe to be the problem is that as this funding has tripled (after adjusting for inflation) over the last 30 years in the United States, the funding for the physical sciences has remained flat over the same period (Fig. 5). However, in 2000, the National Nanotechnology Initiative (NNI) was launched by the United States govern-

ment with great fanfare. Similar programs had already been initiated in other countries. At least in this sector of the physical sciences, the funding is increasing at a rapid rate. Just 2 years after the beginning of NNI, the total annual expenditures were nearly \$600 million in the US, with by far the largest portions going to three agencies, the National Science Foundation and the Departments of Defense and Energy. Such funding shifts have not been seen within the physical sciences for many years, and the dramatic increase in funding nanoscience and technology by the US and other governments is just another indication of the young, but clearly recognizable revolution that we are in.

7. What lies ahead

It is widely anticipated that the future impact of nanotechnology will eventually far exceed the impact of the silicon-based integrated circuit (i.e. computer technology as we know it today). This is because nanoscience has applications in all areas of science, and nanotechnology has application to all fields of technology, computing and otherwise. Like the present biological science revolution in genomics and proteomics, the importance of the nanofield is so sweeping, so vast, that no boundaries can yet be reliably defined, and no limits can yet be clearly foreseen. Scientific historians know all too well that technology predictions are notoriously inaccurate. In the March 1949 edition of the still popular and respected magazine *Popular Mechanics*, appearing shortly after the invention of the solid state transistor at Bell Labs, experts published predictions of futuristic calculators (computers) that would add 5000 numbers per second and weigh only 1400 kg or so while consuming 10 kW of power. Today, a 1 kg laptop can add millions of numbers per second using about 1 W of power. So who can reliably say today what a quantum computer, based on nanoscience and technology, will be able to do in the future, or what fields will be most dramatically impacted by nanoscience in the future? What is certain is that nanoscience and technology will make an impact on every scientific field,

and it is very likely that this impact will be fundamental and significant over time.

Clearly, the field of Earth and planetary sciences will not be excluded from this revolution. Nanosized Earth materials are ubiquitous in nature, not only as individually definable particles, but as thin films of solids and fluids and as nanoscale domains and features within and on minerals. Mineralogical, geochemical, and geophysical properties such as stability ranges, solubilities, sorption and redox behaviors, reaction kinetics, conductivity, rheology, magnetism and others can be specifically measured and/or modeled for Earth solids with one, two, or three dimensions in the nanodomain. Large differences relative to the same or similar phases, but coarser, should be expected. Indirectly, new types of computers, including quantum computers, and new sensors/detectors based on rapidly emerging nanotechnologies will almost certainly have major impacts on how we model and analyze the Earth and planets.

The ultimate rewards in this currently unfolding story will be at least two-fold. The first is obvious in gaining a more complete understanding of many Earth and planetary processes. But the second may be ultimately more important. This will be in the applications of both new knowledge and spin-off technologies towards sustainability issues right here on planet Earth [41].

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