Mineralogy, materials science, energy, and environment – A 2015 perspective

Alexandra Navrotsky

1Peter A. Rock Thermochemistry Laboratory and NEAT ORU, University of California, Davis
Davis, CA 95616

Abstract

Mineralogy is both a basic and applied discipline, basic in understanding, on the atomic scale, the structure, properties, and reactivity of minerals and applied in its relevance to geology, planetary processes, environmental issues, and materials in the broader sense. This article is a 2015 snapshot of the interrelations and opportunities linking mineralogy and such other fields. The emphasis is on showing how relevant, indeed essential, mineralogy is to the stewardship of our planet in the broadest sense.

Introduction

Mineralogy has always been inspired by the beauty of minerals and their structures and the wonder of the natural world. At the same time it has been nourished by practical applications - all inorganic materials we use in technology, from Stone Age spear points to silicon age semiconductors, come from minerals. Think of it, the guts of your cell phone started as sand, with dabs of iron ore, rare earth minerals, and lots of organic compounds derived from petroleum. If we run out of these ingredients, or if we soil our surroundings with their production and disposal, we are in trouble. Thus knowledge of mineralogy forms the underpinning, not just for technological advancement and big bucks, but also for stewardship of our planet. Realizing our responsibility as scientist citizens as well as researchers, I write this review to point out the symbiotic relationships among mineralogy, technology, and environmental issues and to highlight opportunities for the future of our field. Though public policy and politics are
inexorably linked to science and technology, they are not a major focus of this paper. Because this article is short, the references cited are not extensive and have been chosen, when possible, to themselves be of a review or overview nature.

Clearly there are many other points of intersection between mineralogy and materials science. Both fields are blurring the distinction between organic and inorganic, with hybrid materials, biomineralization, microbial synthesis of technological materials, and the use of functionalized nanoparticles in medicine being some areas of active interest. Both fields utilize magnetic properties for functionality and indication of sample processing or geologic history. Both are increasingly cognizant of environmental impacts and the role solids (industrial pollutants and natural minerals) play in catalyzing and directing chemical reactions in both aqueous and atmospheric environments. The present paper presents only a few examples of such commonality.

The Porous Interface between Mineralogy and Materials Science

Both mineralogy and materials science study solid inorganic compounds - oxides, silicates, chalcogenides, carbonates, carbon polymorphs, sulfates, halides and others. Both fields determine structure, physical properties, and stability of the materials. The main goal of mineralogy as part of earth science is to use such fundamental knowledge to better understand the conditions of formation of the minerals through space and time, with pressure as well as temperature being major variables. Mineralogists consider slow processes occurring on a geologic time scale as well as processes occurring in the laboratory. The goal of materials science, broadly speaking, is to use basic knowledge of solid state compounds and their properties to design and tailor materials with technologically useful functionality. Minerals are often complex solid solutions containing many elements at major, minor, and trace...
concentrations. Materials are synthesized at controlled and usually simple compositions, with impurities (dopants) intentionally introduced to fine-tune properties such as electrical conductivity. Despite these differences in emphasis, the two fields share many commonalities. Both often study similar families of materials, e.g. perovskites, spinels, garnets, zeolites, iron and manganese oxides. Both fields require fundamental understanding of structure, bonding, and thermodynamic properties. Both make use of modern experimental and computational methodologies. With these commonalities in mind, this review points out areas of overlap, synergy, and complementarity and opportunities for future interactions.

Concepts, Techniques, Centers

A simplistic picture of the relation between mineralogy and materials science is that the mineralogist sits at the feet of the solid state physicist to learn fundamental concepts and to take advantage of modern instrumentation. The reality has always been much more of a two way street, with mineralogy (or mineral physics) leading the way in a number of areas. Historically, the needs of the lunar science program accelerated the development of the electron microprobe and other instrumentation. Mineralogists have been at the forefront of electron microscopy since the 1970s. The most obvious direction in which mineralogy leads is in the application of pressure as a variable, absolutely necessary to understand planetary interiors. Diamond anvil cell (DAC), methodology has grown to span conditions from shallow hydrothermal systems to the center of the Earth (Bassett 2009). At the same time the development of multianvil press technology, first in Japan and now worldwide, has led to tremendous advances in synthesis and property measurements of phases under mantle conditions (Liebermann 2011). Hand in hand with high pressure development has been the invention of diagnostics suitable to very small sample
volumes - especially diffraction and spectroscopy utilizing synchrotron radiation (Liebermann 2011). Thus the mineralogy community has led the development and operation of synchrotron beam lines for high pressure research. This mineralogical emphasis on high pressure led to the NSF funded Science and Technology Center in High Pressure Research (CHiPR) which functioned for eleven years (1991-2002) and to its successor, COMPRES (Consortium for Materials Properties Research in the Earth Sciences), currently providing support for mineralogical synchrotron research and related projects.

Several DOE (Department of Energy) Energy Frontier Research Centers (EFRC), led by mineralogists or geochemists were funded in 2009-14 and recently renewed for the next four years. The EFRCs (46 centers in 2009-14 and 32 in 2014-18) emphasize fundamental multidisciplinary collaborative research with eventual energy applications. The strong participation of the mineralogy/mineral physics community in these highly competitive centers is testimony to the high quality of our research and offers unique educational opportunities for students, postdocs and faculty.

Shock wave research (Jeanloz et al. 2007; Ahrens et al. 2009) probes an even wider set of planetary conditions and also forms a bridge between planetary science, national defense interests, materials science, and cosmology. It is part of a broader field known collectively as high energy density science (HEDS) which is being propelled forward by technological advances such as the National Ignition Facility (NIF) at Lawrence Livermore National Laboratory (Moses et al. 2009) and new free electron laser facilities worldwide. HEDS spans a pressure regime from planetary interiors to stars to nuclear explosions and brings together mineral physicists, planetary scientists, material scientists, cosmologists, and nuclear physicists.
Mineralogists continue to take advantage of developments in crystallography, revolutionized by ever-increasing computer power. The ability to perform single crystal refinements on ever smaller crystals, the combination of synchrotron and neutron experiments (and in some cases simultaneous fitting of data), the emphasis on whole powder pattern fitting including diffraction intensity between Bragg peaks, which gives information on disordered solids – all these enable efficient solution of previously intractable problems (Ehm et al. 2007; Parise 2006; Skinner et al. 2013;). Electron microscopy continues to prosper, with high resolution compositional analysis an exciting development (Botton 2007; Kotula et al. 2014; Sanchez et al. 2010; Walther et al. 2014). X-ray spectroscopies probing local and short range order continue to develop (Beyer et al. 2014; Chapman and Chupas 2013). Yet describing structure and partial order on the 1-100 nm scale still remains challenging. Neutron scattering and diffraction techniques have improved greatly, requiring much less sample and providing crystallographic, magnetic and vibrational data (Loong 2006; McMahon 2012; Redfern 2002; Ross and Hoffmann 2006). The sensitivity of neutrons to light elements, including hydrogen, makes them complementary to X-rays. In situ studies at high temperature and/or high pressure are an emerging frontier for both mineralogical and materials studies.

Another area of mineralogical leadership is in structural, kinetic, and thermodynamic characterization of reactions at the solid - aqueous interface. Earth scientists have pioneered neutron and synchrotron-based spectroscopic and diffraction techniques to study such reactions and have closely coupled experiment and computation (see, for example Fenter et al. 2007; Kumar et al. 2009; Spencer et al. 2009; Strongin et al. 2010; Wang et al. 2014; Zhang et al. 2014). Mineral dissolution and precipitation occurs at the mineral-water interface, and the processes controlling both dissolution and precipitation often involve nanoparticles and clusters.
Mineralogists have led the way in realizing that there is a continuum between dissolved aqueous ions, polyoxometallate and carbonate clusters in solution, amorphous and crystalline nanoparticle precipitates, and bulk solid phases (Gebauer and Côelfen 2011; Nyman and Burns 2012; Ohlin et al. 2010; Radha and Navrotsky 2013; Rustad and Casey 2012). Such understanding is crucial not just for geochemistry and environmental science but for the many industrial processes which occur in aqueous environments, often at somewhat elevated temperatures. These include materials synthesis (including of zeolites for catalysis in the oil industry), catalysis itself, CO₂ sequestration, and the longevity and degradation of devices such as batteries, fuel cells, and sensors.

The mineralogical/geochemical community has long used isotopes to date rocks and study their sources. Recent advances which simultaneously enable chemical and isotopic compositions to be determined with high spatial resolution (Ferry et al. 2014, Valley et al. 2014) open new opportunities to follow mineral reactions at the nanoscale, probe equilibrium or lack thereof, and study kinetics. These methods are barely known to the materials community, yet would find many applications there.

A wealth of new materials has been created by materials scientists. Using techniques involving low temperature processing, vapor phase deposition, ion exchange, and various precursor routes, metastable materials can be explored and applied. Freed from the “tyranny of equilibrium”, one is able to access not just the lowest free energy phase assemblages, but a dense energy landscape of only slightly metastable structures. Such new materials have unique optical, electronic, magnetic, and catalytic properties. Two examples of new classes of materials are superconductors with high critical temperatures (Oesterreicher 2007; Ren and Zhao 2009; Tretyakov et al. 2004), and silica zeolites and mesoporous materials (Asefa and Tao 2012;
Broach 2010; Han and Zhang 2012; Li and Yu 2014). This emphasis on metastable materials puts new focus on seeking and characterizing metastable natural materials, for example the myriad polymorphs of manganese and iron oxides, which in turn may have useful properties. At the same time the focus on other planets both in the solar system and beyond (Buchhave et al. 2014), has freed mineralogists from the “tyranny of Earth’s geotherm and composition”. Mineralogists are no longer constrained to think only within the pressure – temperature – composition parameter space on Earth, but can contemplate very different planetary conditions and new materials - lakes of hydrocarbons, planets with diamond-rich interiors, high energy density interiors verging on nuclear fusion, interior water-rich oceans below icy surfaces, the harsh conditions for dust grains in space -to name a few. Is this a renaissance for petrology?

New materials and minerals require new data, including thermodynamic properties. Commercial thermal analysis equipment has expanded to fill a wider temperature range and many instruments combine measurements to include not just mass and heat as a function of temperature (classical TGA-DSC) but also evolved gas analysis (EGA) by mass spectrometry or infrared spectroscopy, structural measurements by X-ray diffraction, and other tandem techniques (Gabbott 2008; Mojumdar et al. 2009). Low temperature heat capacity measurements, needed to obtain standard entropies of phases have been made much more accessible, both in terms of smaller sample size and more rapid measurement, through the Quantum Design PPMS system, with specific techniques developed to handle small amounts of powdered mineral samples (Dachs and Benisek 2011; Shi et al. 2011). The high temperature Calvet twin microcalorimeter used for heat of formation measurements by oxide melt solution calorimetry, previously only home-built, has been commercialized as the Setaram AlexSYS (Levchenko, et
Experimental thermodynamics is poised for a renaissance, both to obtain needed data on new materials and to interface with computational studies, including the national Materials Genome Initiative, EarthCube, and other “big data” endeavors.

A number of workshops have been held in the materials community, and recently in the geoscience community related to the Materials Genome Initiative. The mineralogical community participates in mineralogical and crystallographic data base projects and is active in the creation of websites and programs for easy retrieval of crystallographic data and depiction of mineral structures for both research and educational purposes. Several thermodynamic databases and associated computational programs for mineralogical systems have been developed and, to some extent, maintained and made more compatible with modern information technology (Asimow and Ghiorso 1998; Boudreau 1999; Gualda et al. 2012). These thermodynamic data bases are different from those used by the materials community (the CALPHAD approach) (Bale et al. 2009; Becker et al. 2014; Campbell et al. 2014; Kroupa 2013) especially in terms of how solid solutions and melts are modeled. The materials community has limited capability to include high pressure in their data bases and computations. Each community has developed data bases and computational capability for aqueous solutions; yet linking complex mineral (or ceramic) phase thermodynamics and aqueous activity models, especially at high temperature and pressure, remains challenging. There is a great opportunity for the materials and geoscience communities to work together.

An even broader challenge is retrieving (data mining) all the known properties of a given material or mineral or ceramic composite or rock, including original experimental data, both recent or in the older literature. It is technologically possible to give any material a code number which would then be used to link it to all other data (or references) on the same material. Should
this be done, how, by whom, paid by whom? These are big data questions for the future in both
earth and materials science. They also have major implications and impacts for the evolving field
of journal publishing. There is no doubt we are living through the biggest communications
revolution since the invention of the printing press.

Below I give several examples of research bridging mineralogy (mineral physics) and
materials science and some outlooks for the future.

**Perovskites**

The perovskite structure (see Figure 1 and Mitchell 2002 for a comprehensive review) is
ubiquitous in both materials and Earth science. Materials scientists are still largely unaware that
MgSiO₃ perovskite may be the single most abundant mineral in our planet, though largely
inaccessible because of its instability at ambient conditions. When I lecture on this topic as part
of a materials science seminar, it is often a “whole new world” to the materials community and
one can hear a pin drop in the lecture hall. Nor are they aware of the detailed high pressure
studies of equations of state and phase transitions that the mineral physics community has
developed and how these are useful in understanding chemical bonding and benchmarking
theoretical calculations. On the other hand, mineralogists still tend to use the term “defect”
qualitatively and ignore the rigorous treatment of defect equilibria developed over many years by
the materials community. Tailoring the defect chemistry of perovskites by ionic substitution
(doping) and control of oxidation state is leading to new perovskite based materials for
applications as diverse as solid oxide fuel cells (Cook and Sammells 1991; Jiang and Li 2009),
water splitting and other catalytic reactions (Cava 2000; Ghinga et al. 2011), separation
membranes (Fontaine et al. 2008), and high temperature superconductors (Dow and Harshman
2002; Park and Snyder 1995) and piezoelectrics (Reany 2007). Of potential importance to the incorporation of water in the deep earth are studies showing that perovskites with oxygen vacancies which are oxide ion conductors can incorporate H$_2$O and become proton conductors (Norby 2009; Norby et al. 2004). Such ceramics may provide analogue compounds for geophysical studies.

The coupling of trivalent ions (Al substituting for Si) may also strongly affect defect chemistry, vacancy concentrations, and water content in deep Earth materials (Navrotsky 1999; Spektor et al. 2011). The discovery based on both theoretical and experimental evidence, of “past perovskite”, namely closely related complex structures related to perovskite having slightly higher density (Hirose et al. 2006; Umemoto and Wentzcovitch 2006; Yamanaka et al. 2012) has disproved the previously common notion that, at high pressure, crystal structures become simpler and more symmetric. The changing spin state of Fe$^{2+}$ at high pressure adds complexity to structure, bonding, and properties at conditions of the lower mantle and core (Badro 2012). Thus high P-T mineralogy (mineral physics) continues to discover new phenomena.

In fine grained (nanophase) materials, additional water incorporation and proton conductivity is associated with grain boundaries (Scherrer et al. 2013). Such observations may help define questions for grain boundary structure and water diffusion in mineralogical systems. In materials science detailed studies of grain boundaries, especially in metals, has led to the concept of “complexions” (Cantwell et al. 2014). These are specific grain boundary structures, seldom more than a few nanometers thick, and having compositions and order different from the bulk material. Different complexions may occur at different grain boundaries in the same material, and they may control transport and reactivity. Though not separate phases, complexions are structurally distinct from their matrix. The ability to characterize these structures and their
compositions by modern electron microscopy opens a new field, probably as important to
minerals as to ceramics.

Current and future new directions in ceramics have been summarized in a recent review
article resulting from an NSF workshop (Rohrer et al. 2012). The challenges and opportunities
described there are clearly applicable to the study of minerals as well.

Nanophase Materials

In the low temperature aqueous environment minerals often precipitate as fine particles
(nanophases) and remain fine-grained without coarsening for long periods of time. Similarly, in
chemical synthesis on a laboratory or industrial scale, initial nanophase precipitates are
amorphous, or poorly crystalline and only gradually transform to coarse grained stable phase
assemblages with heating. Nanomaterials of interest to both mineralogy and materials science
include aluminum and iron oxides, titania, and silica. Deposition of solids from a dilute gas
phase in technological processes such as chemical vapor deposition and precipitation of mineral
phases from a dilute gas phase in the early solar system may share common features, particularly
the initial formation and persistence of fine grained (nanophase) precipitates different in structure
and properties from bulk materials. A recent development is the realization that differences in
surface energies between different phases adds a term to the free energy of reaction in the
nanoregime large enough to lead to crossovers in polymorph stability and shifts in the P-T
locations of both dehydration and redox equilibria when the system is constrained from
coarsening (Navrotsky 2011; Navrotsky et al. 2008, 2010). An example for manganese oxides
(Birkner and Navrotsky 2012) is given in Figure 2. This interplay of thermodynamics and
kinetics, with thermodynamics playing a larger role than previously thought, has implications for fields ranging from catalysis to soil science.

Confinement and Host-Guest Interactions

It is becoming increasingly clear that molecules confined near a solid surface interact strongly with it and exhibit different properties from the same molecules in an unconfined state (Gubbins et al. 2011, 2014; Srivastava et al. 2011; Werner et al. 2014). The solid surface may be roughly planar or it may be strongly faceted or curved. Confinement may occur in two dimensions (at a mineral-water interface) or in three (inside a pore). In the latter case one calls the porous material the host and the confined molecules the guest. The pores may be of specific sizes and arranged in a periodic array within a crystalline material (see Figure 3), such as a zeolite, mesoporous material, or metal organic framework (MOF) (Davis 2014; Furukawa et al. 2013; Lehman and Larsen 2014; Valtchev and Tosheva 2013). Pores may be separated and relatively inaccessible or bridged by channels with “windows” of a given size connected in one, two, or three dimensions. The pore walls may be amorphous but the channels arranged with uniform spacing, as in mesoporous silicas, or pores may exhibit a narrow range of sizes with random geometric distribution, as in controlled pore glass (CPG). Finally there may be a wide distribution of pore sizes and geometries, as in real ceramics and rocks. The systems with simpler and better characterized pore distributions are valuable models for the more complex “real world” systems. Over the past decade the materials community has been able to synthesize, characterize, and model many such controlled pore materials and begin to understand, at the molecular level, the dynamics of confinement. These same materials offer opportunities for mineralogists to study confinement phenomena relevant to earth science, including the effect of
temperature and pressure over wider ranges than of usual interest to the materials community


Though H₂O is the most common guest molecule, others are of importance to both mineralogy and materials science. Chief among these are CO₂ in the context of carbon dioxide capture and sequestration and CH₄ in the context of natural gas (de Paolo et al. 2013; Guyot et al. 2011). In the suite of DOE EFRCs funded from 2009 to 2014, two concerned CO₂ sequestration and one CO₂ capture by MOFs have been renewed and one more added for the next four years. Collaboration between mineralogy, materials science, and petroleum engineering is needed to understand and improve enhanced oil recovery, hydraulic fracturing (“fracking”) and long term CO₂ sequestration.

Both CO₂ and CH₄ figure prominently in the global carbon cycle in the earth’s interior and a large international project, the Deep Carbon Observatory (DCO) funded by the Sloan Foundation brings together research in this field. The scope is broad and includes mineralogy, petrology, and mineral physics. A focus is how carbon is incorporated in the mantle and core, with many unanswered questions as to both the amounts of carbon in these reservoirs and its mineralogical form. Nanodiamonds and other carbon allotropes (Gogotsi and Presser 2014), the incorporation of carbon into solid and molten silicate phases, possibly as C substituting for O rather than Si (Sen et al. 2013), represent additional interfaces between mineralogists and materials science researchers.

Strategic and Critical Materials

There is growing concern at many levels of government that our technology is vulnerable both to real scarcity and to geopolitical constraints in the availability of so-called critical elements (Normile 2010). These include the rare earths, lithium, tellurium, and others. From the
point of view of mineralogy, important rare earth minerals, or phases into which rare earths
substitute, include bastnäsite, monazite, pyrochlore, and apatite. Lithium comes largely from
pegmatite minerals. The demand for rare earths in electronics, cell phones, lighting (LEDs),
magnets, and other applications is increasing rapidly, while the growth of the lithium ion battery
threatens to outstrip supply, especially if such batteries become commonplace in automobiles.

Our vulnerability can be minimized at many different levels: more efficient and environmentally
friendly mining and ore processing; finding substitutes or using less of a critical material for a
given device; recycling. The National Science Foundation has identified Sustainable Chemistry
(SUSchem) as an internal initiative and the Department of Energy has established a “Hub”, the
Critical Materials Institute, a large program spanning from basic science to industrial
intervention and involving national lab, academic, and industrial partners. Because all critical
materials come from the Earth and are eventually returned to it as waste, it is clear that
mineralogists, materials science researchers, and industry must work together to achieve goals of
sustainability in critical materials. Though the details will evolve, these issues will be with us for
the foreseeable future.

The Nuclear Fuel Cycle
Whatever the long term future of nuclear energy, electricity-producing reactors will be
active in many countries for many years to come, and the safe disposal and stewardship of
nuclear waste remains a major issue. (Weber et al. 2009). Natural uranium minerals (uraninite
and various complex $\text{U}^{6+}$ uranyl phases) are mined and processed into nuclear fuel, usually $\text{UO}_2$.
After use in a reactor, the fuel rods (“spent fuel”) are either reprocessed or stored. Safe storage,
whether on the surface or in an underground repository, requires the minimization of corrosion and dissolution of UO₂. Earth scientists, materials scientists, and nuclear engineers must work together, and all must work within the geopolitical and policy context to make progress possible. The expertise of mineralogists in solving complex crystal structures has expedited the characterization of the structures of the myriad of uranyl minerals and recently discovered uranium peroxide cluster compounds (Burns 2010; Nyman and Burns 2012). Their reactivity in the environment is critical to understanding uranium transport, including after a reactor accident (Burns et al. 2012). As one considers repositories other than Yucca Mountain for nuclear waste, there is need for much additional work. The recent incident at WIPP, the Waste Isolation Pilot Project in salt formations in New Mexico, highlights the need for additional careful research of waste behavior in different geologic environments. New reactor designs (e.g. small modular accident resistant reactors) and different fuel cycles (e.g. the thorium-based cycle) all require new interdisciplinary collaborations.

Outlook

The study of earth materials is evolving to include a much broader spectrum of societally relevant problems and to utilize a more diverse palette of experimental and computational approaches. Our stewardship of a sustainable planet requires deep understanding of geochemical cycles both in the critical zone and in the whole planet. Technology relies on minerals as sources of common, rare, and critical elements and eventually returns these elements to the environment. The richness of mineralogy in extraterrestrial environments is just beginning to be appreciated. Life depends on minerals and influences their formation and transformation. Indeed minerals change through geologic history, and mineral evolution and the emergence of life may be closely
connected (Hazen and Papineau 2012). As mineralogists in the 21st century, we have the good fortune of working in a broad field of both marvelous intellectual challenge and critical societal importance. Our challenge is to choose the most important problems, work with our colleagues in a variety of disciplines to solve them, and to educate the public at all levels as to why understanding materials in the Earth is critical to sustaining both our standard of living and the planet as a whole.

References


Buchhave, L. A., Bizzarro, M., Latham, D. W., Sasselov, D., Cochran, W. D., Endl, M.,
Chimie, 13, 737-746.
335, 1184.
generation CALPHAD. Scripta Materialia, 70, 7-11.
Chapman, K. W., and Chupas, P. J. (2013) Pair distribution function analysis of high-energy X-
ray scattering data. In J. A. Rodriguez, J. C. Hanson, and P. J. Chupas, In-Situ
Characterization of Heterogeneous Catalysts, p. 147-168, John Wiley & Sons, Hoboken,
New Jersey.
Davis, M. E. (2014) Zeolites from a materials chemistry perspective. Chemistry of Materials, 26,
239-245.
dePaolo, D. J., Cole, D. R., Navrotsky, A., and Bourg, I. C., Eds. (2013) Geochemistry of
Geologic CO₂ Sequestration, vol. 77, 539 pp. Reviews in Mineralogy and Geochemistry,
Mineralogical Society of America, Chantilly, Virginia.

Dow, J. D. and Harshman, D. R. (2002) Explanation of high-temperature superconductivity
without cuprate planes. Philosophical Magazine B, 82, 1055-1066.


hydrogen separation membranes based on dense ceramic conductors. Membrane Science and Technology Series, 13 (Inorganic Membranes), 401-458.

Furukawa, H., Cordova, K. E., O’Keeffe, M., and Yaghi, O. M. (2013) The chemistry and


approach to the structure of liquid alumina. Physical Review B: Condensed Matter and
Materials Physics, 87, 024201/1-024201/16.

Spencer, E. C., Levchenko, A. A., Ross, N. L., Kolesnikov, A. I., Boerio-Goates, J., Woodfield,

P., and Häussermann, U. (2011) Ultra-hydrous stishovite from high pressure
hydrothermal treatment of SiO₂. Proceedings of the National Academy of Sciences of the


precipitation controlled by surface chemistry. Environmental Science & Technology,
102, 6177-6183.

environmentally relevant iron (oxy) hydroxides ranging from the nano to the macro-

microstructural features of functional materials based on cuprates and manganites.
Russian Chemical Reviews, 73, 881-898.


adsorption at the rutile-water interface: Linking molecular and macroscopic properties.

Langumir, 20, 4954-4969.
Figure Caption

Figure 1 The perovskite structure, stoichiometry ABO$_3$, consists of a linkage of BO$_6$ octahedra sharing corners. The volume defined by the interstices formed by this linkage contains a large B cation, depicted here as the Earth to show the importance of this structure for mineral physics and geophysics. For smaller A cations, the octahedra can tilt, as shown, lowering the symmetry from cubic to tetragonal, orthorhombic or monoclinic.

Figure 2 “Phase equilibria in the Mn-O system for (left) bulk materials and (right) 10 nm hydrous nanoparticles. Note expansion of stability field of the spinel, Mn$_3$O$_4$ (hausmannite) at the nanoscale. These shifts in phase boundaries reflect the influence of surface energy for high surface area materials. The surface energy of Mn$_3$O$_4$ (the spinel hausmannite) is lower than those of Mn$_2$O$_3$ (bixbyite) and MnO$_2$ (pyrolusite). Thus the spinel (with both Mn$^{2+}$ and Mn$^{3+}$) is thermodynamically stable to higher oxygen fugacity at a given temperature for small particles. (Birkner and Navrotsky 2012). The uncertainties in calculated pressures at a given temperature are on the order of 0.1 log unit, so the shifts for nanoparticles are far beyond experimental uncertainty.”

Figure 3 Energetics of zeolites, mesoporous silicas and metal organic frameworks (MOF) relative to dense phase assemblages as a function of molar volume. It is striking that a large increase in volume (over a factor of two) caused by the formation of open channels and cages, has a relatively small energy penalty (<30 kJ/mole). This energetic accessibility accounts for the large number of possible structures, described as a “dense energy landscape” (Hughes et al. 2013).
Figure 1
Figure 2
Figure 3