APS Midterm Renewal: Science Justification Geological, Environmental, and Planetary Sciences

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## 1. Executive Summary

The availability of third-generation synchrotron radiation at the Advanced Photon Source has enabled noteworthy progress across a wide spectrum of problems in the geological, environmental, and planetary [GEP] sciences. Formally, GEP science at the APS comprises about 15% of the user base, and has significant growth potential, but it is also highly interdisciplinary and experiments in physics, chemistry, and materials science (e.g., in extreme conditions) are often carried out to address problems in these areas. One key characteristic shared by GEP sciences is the complex nature of the materials involved in their phenomena, which occur over extremely broad ranges of length and time scales as well as temperature and pressure. At the foundation are the molecular-scale structure, composition, and reactivity of the constituent phases. These scale up differently, depending on the systems in question, to produce a rich palette of large-scale behaviors that are difficult to understand without knowing the molecular-scale fundamentals. Thus it is crucial to have access to facilities such as the APS to be able to continue advancing scientific progress in these areas. Some of the factors that limit this progress are as simple as the number of available beamlines, the flux and brilliance of the available beamlines, and the quality of available X-ray optics and X-ray detectors. Also, full use of the APS by GEP scientists requires more beamline personnel who could contribute to designing and running experiments, and more ancillary experimental hardware including sophisticated sample chambers capable of maintaining controlled conditions of pressure, temperature, and fluid composition. Additional laboratory space for staging the increasingly complex experimental preparations should also be made available.

### 2. Introduction

Mankind's continued inhabitation of planet Earth will depend increasingly on strategic stewardship of our natural resources. Sustainable use of energy and raw materials, with minimal environmental damage, is imperative to ensure a viable quality of life for Earth's inhabitants. However, only with an adequate understanding of the structure, composition, and function of natural systems, at scales ranging from atomic to global, can we accurately predict and control the environmental consequences of our actions. The requisite levels of understanding for this have not yet been achieved in the GEP sciences. In addition, there are many new opportunities for planetary science,

driven by direct sampling missions of other bodies and observational discoveries that include planets far beyond our own solar system. Further progress is limited by the availability of scientific tools capable of measuring the atomic- to cm-scale properties and behavior of natural materials *in situ*, in real time, and under a wide range of conditions. An exceptionally powerful set of tools for such investigations is provided by high-brilliance synchrotron radiation facilities. Experiments performed at these facilities have led to new findings and conceptual advances of fundamental importance. Improvements in the spatial and temporal resolution of synchrotron X-ray measurements, as well as increases in sample throughput, will be enabled by new X-ray optics and detectors. These improvements will lead to wider use and ever more powerful applications of synchrotron radiation to make new discoveries and develop new theories in the GEP sciences.

## 3. Key Science Drivers

The GEP sciences encompass a wide range of multifaceted topics that frequently transgress conventional disciplinary bounds. Much of the forefront research in these fields has a clear relevance to applications in energy-related activities, as described in the workshop reports produced by DOE's Office of Basic Energy Sciences, Basic Research Needs for Geosciences: Facilitating 21st Century Energy Systems (2007) and Research Needs for Materials under Extreme Environments (2008). Synchrotron radiation techniques have become essential tools in such research, because of their strengths in characterizing complex materials over a range of length scales and X-ray energies. Classic scientific questions of geology and planetary science are also being addressed using synchrotron radiation. High-priority science targets under investigation at the DOE synchrotron radiation facilities include mineral-water interface complexity and dynamics, nanoparticle reactivity and transport, trace element mobility and distribution, biogeochemistry in the subsurface, high-pressure mineral physics and structure of the Earth and planetary 's interiors; cosmochemistry and planetary geochemistry; and life in extreme environments and the origin of life. Brief descriptions follow of the driving questions and methods employed in each of these areas, with reference to the limitations imposed upon such research by the available hardware at the synchrotron radiation facilities.

## Mineral-fluid interface complexity and dynamics

The mineral-fluid interface is the principal site of geochemical reactions at and near Earth's surface. Mineral-fluid interface processes exert a powerful influence on the natural geochemical and biogeochemical cycles in our environment. These processes are crucial in the diagenesis of sediments and weathering of rocks, in the formation of ore deposits and petroleum reservoirs, and in soil formation and plant nutrition. Mineral-fluid interface processes effectively control the compositions of groundwaters, surface waters, the oceans, and, to a large extent, the atmosphere. These processes are integral to vital aspects of the dynamic natural world in which we live; in many practical ways, our lives depend on them. Minerals also have critical applications in technical fields such as construction, manufacturing, ceramic synthesis, catalysis, gas and liquid separations,

water and wastewater treatment, waste disposal, agriculture, and horticulture. For these reasons, we must improve our fundamental understanding of mineral-fluid interface processes to make efficient and intelligent use of our natural resources and to protect the quality of our environment. Only by quantifying these processes at the molecular scale will we be able to predict behaviors in a wide range of geological and environmental systems. Examples of such complex systems include contaminant transport in groundwater aquifers, interaction of complex crustal fluids with rocks, the consequences of deep injection of CO<sub>2</sub> into depleted oil and gas reservoirs, the extraction of geothermal energy from hot rock, and the long-term isolation of high-level nuclear waste.

Much of the recent work on mineral-fluid interfaces and mineral surfaces began by applying experimental and theoretical techniques first used by scientists studying other materials (e.g., catalysts and semiconductors). Despite significant experimental and theoretical efforts in the past decades, understanding of the actual molecular-scale geochemical processes (including adsorption, dissolution, growth, and precipitation) remains poorly constrained by direct observations in most cases. The current state of knowledge is limited by the intrinsic complex nature of geochemical interfaces and the great difficulty of probing mineral-water interfaces in situ at the molecular scale. The advent of the atomic force microscope (scanning probe microscopies?) and the development of non-linear optical and synchrotron X-ray techniques have initiated new classes of in situ nanoscale and atomic-scale studies of mineral-fluid interfaces in the past two decades (Binnig et al, 1986; Ohnesorge and Binnig, 1993; Shen, 1994; Hochella and Banfield, 1995; Brown and Sturchio, 2002; Fenter, 2002; Bedzyk and Cheng, 2002). Meanwhile, computational advances have enabled more sophisticated theoretical understanding of mineral surface properties (Cygan and Kubicki, 2001). Now that these experimental and computational approaches have matured to a point where they can be applied to a common and representative system size, they have begun to be used synergistically to test our understanding of mineral-fluid interfacial systems (e.g., Cheng et al., 2001 vs. Park and Sposito, 2002; Geissbuhler et al., 2004 vs. Kerisit et al., 2004; Trainor et al., 2004). Quantitative agreement between experimental observations and theoretical predictions provides a non-trivial confirmation of our understanding, while contradictions, in turn, suggest that our understanding is inadequate.

The over-arching goal of future research is to develop fundamental comprehension of mineral-fluid interfacial processes through direct observation of interfacial structures and dynamic processes at the molecular scale. New conceptual understanding will provide answers to questions such as: What controls the reactivity of a mineral surface? What is the actual structure of the mineral-fluid interface? How do ions and organic macromolecules adsorb to charged mineral-water interfaces? How do minerals dissolve and grow? Ultimately, the ability to improve the predictive capability of geochemical transport models, and to relate fundamental molecular-scale processes to field-scale behavior, relies on the development of appropriate theories that are validated through direct, in situ observations. Improvements in the flux and brilliance of synchrotron radiation sources, along with improved X-ray optics and detectors, are essential for making progress in this area.

# Nanoparticle reactivity and transport

Natural nanoparticles are ubiquitous within the earth, at its surface, and beyond its surface, and have specific importance in certain GEP processes. They can form in geomicrobiological reactions, at mixing fronts of highly supersaturated contaminant plumes with ground water, during rock weathering, in the rhizosphere, in smokestacks from coal-burning, in subsurface sedimentary rocks, and in the cosmos. surface their formation, disappearance, and mobility affect the quality of our water, air, and soil and hence the viability of life. Natural nanoparticles can be purely inorganic, organic, or a mixture of both. They may be relatively impure in contrast to engineered nanoparticles and have proteinaceous (Moreau et al., 2007) or dissolved organic matter coatings. Their suspension in flowing air or in surface and ground water can rapidly mobilize contaminants that either compose the nanoparticles or are adsorbed on other nanoparticle substrates, a problem designated as a priority research direction in the geosciences by the recent DOE Basic Research Needs in Geosciences report (DOE, 2007). Deep in the earth, nanoparticles may form at and subsequently control rock motion along faults, which generates earthquakes at the surface (Green and Burnley, 1989; Wilson et al., 2005). New engineered nanoparticles synthesized for technology developments ultimately may contact and interact with earth surface environments (water, air, biogeosystems) in unpredictable ways. Given this burgeoning attention to nanoparticles, we must rapidly expand our knowledge of how they form; their compositions and structures; how their surfaces react chemically in bulk fluids and when coated with thin fluid films; how they move in bulk fluids, in fluids confined by grain boundaries or pore throats, or gaseous atmospheres; and, how they aggregate and/or grow to larger size. Observations must pertain to the chemically and structurally complex range of natural environments in which nanoparticles exist.

Recent advances in characterization approaches, for example use of high energy X-ray scattering to extract nanoparticle structures at correlation length scales beyond the range of X-ray absorption spectroscopy, are providing new insight to formation and transformation processes relevant to geoscience questions (Soderholm et al., 2008; Michel et al., 2007). Such data will allow development of a thermodynamic description for particles that bridge the size gap between aqueous complexes and micrometer-scale crystallites (Navrotsky et al., 2008). At this range of molecular scale the lack of a general theory is severely stalling advancement in understanding the phase chemistry and kinetic behavior of natural nanoparticles. Information that is only accessible by high energy Xrays is essential for theoretical progress. Synchrotron microprobe analyses of complex natural materials such as soils and sediments have proven remarkably valuable in identifying associations between contaminants and particular compositional and structural components that lead to new understanding of processes involving nanoparticles (Manceau et al., 2002, 2008; Catalano et al., 2004) despite the micrometerscale spatial resolution that is currently attainable. However, these advancements in multicomponent analyses must be extended to the nanoscale and to trace concentrations to have an impact on fundamental understanding of how nanoparticles influence the fate and transport of environmental contaminants. Both structural and compositional measurements of experimental and in-situ natural nanoparticles must also be accomplished at other than ambient conditions to reflect the range of geo- and planetary environments in which they occur. For these purposes, X-rays will have to penetrate different containment materials.

Understanding the composition, structure, and reactivity of natural nanoparticles will have a significant impact on fundamental knowledge of many Earth and cosmological processes. At the same time, new knowledge of nanoparticle behavior in the environment is critical for addressing the important issue of human sustainability. For example, if we can understand natural nanoparticle formation and stability under stress conditions, we can make progress in understanding when and where earthquakes occur. If we can characterize nanoparticles and their transport in porous media, we will have a significant but currently missing component for models of contaminant ground water flow. If we could characterize small numbers of target atoms on the surfaces of a few nanoparticles, we would better understand the processes that control the environmental distribution of contaminants at the low concentrations considered toxic to human health. Greater access to high-energy X-ray scattering facilities, dedicated microand nanoprobes, and improved detectors and optics are essential to make the needed advances.

# Trace element speciation and incorporation

Trace elements are often the targeted concern in environmental studies. They are commonly risk-drivers at remediation sites or rate-limiting factors in biogeochemical systems. They can have important health consequences when they enter the food chain. For example, Fe in seawater is present at trace levels and is considered an important limiting factor for biological uptake of CO<sub>2</sub> by the oceans. Mercury in aquatic systems can be methylated by bacteria, and then consumed in succession by phytoplankton, fish, and mammals, including humans. The critical concern is that trace elements are present in concentrations that are difficult to study by most techniques. This is especially true when samples must be studied under natural conditions, such as in anaerobic or aqueous environments. Synchrotron radiation analyses are capable of being used to determine key properties of trace elements such as their chemical form and location in complex heterogeneous systems, but only at concentrations typically much higher than their critical levels. Improved capabilities are sorely needed to attain lower detection limits and for time-resolved studies of mineral-water interface reactions, 3-dimensional transport in porous media, and biogeochemical processes.

Many of society's most pressing environmental challenges require detailed knowledge of trace element behavior. At DOE sites the important trace elements are fission products, actinides, and hazardous metals such as Cr and Hg. Elsewhere hazardous trace elements range from As and Sb in mine tailings to heavy metals at industrial sites. Knowledge of trace element speciation and incorporation in field samples is needed to predict future transport and bioavailability, information critical to making intelligent remediation choices. Predictions often also require detailed measurements in the laboratory of surface reactions, biofilms, and inter- and intragranular micro-

environments. Thus, researchers are often faced with the technically challenging requirements of measuring very low concentrations in very small regions.

For example, arsenic can enter the environment through natural processes, mining activities, and pesticide use. Disastrous consequences ensue once arsenic enters water supplies or the food chain, as observed in Bangladesh and West Bengal. Arsenic's many chemical forms (organic or inorganic, As(V) or As(III)) have varying degrees of toxicity, mobility, and bioavailability. Traditional chemical extractions may not retrieve all of the As and can change speciation. In situ speciation techniques using synchrotron radiation have become essential in establishing the human health risks in many studies.

At the APS, trace elements are analyzed using techniques such as bulk XAFS, microprobe-based fluorescence mapping and tomography, micro-XAFS, and surface diffraction on model systems. Diffraction and micro-diffraction can be used to identify the host materials. The microprobe-based methods are most widely used since samples are usually heterogeneous and full-field imaging methods lack the needed sensitivity to ppm levels. With the APS upgrade there is the opportunity to improve current microprobes through improved optics and detectors, which will provide smaller more intense beams. Improved detectors such as large arrays of spectroscopy caliber detectors will be needed to take full advantage of these beams. The net result could be more than an order of magnitude increase in data collection efficiency. More dilute trace element concentrations will become measurable, and the study of larger numbers of samples will be possible. Currently, long data acquisition times restrict investigations to at most a few imaged areas in a few samples. The critical question is then, how representative are these regions of the whole complex environmental system?

# Biogeochemistry in subsurface environments

Microorganisms can control the redox state of major and minor constituents in soils and subsurface environments, and biogeochemical reactions can affect the mobility and bioavailability (i.e., cycling) of most elements in the periodic table. Understanding biogeochemical cycling of elements requires information about the relationships between the metabolic processes and cellular microenvironments of microbial species and the reactivity of solid and liquid geochemical phases. Biogeochemical cycling affects element sequestration, release, precipitation, and solubility; organic complexation and degradation; and, other chemical modifications of contaminants and mineral surfaces. A deeper understanding of the complex reactions that control biogeochemical cycling from atomic to global spatial scales will enable scientists to address areas of concern as diverse as global warming, production of alternative energy feed stocks and their conversion to fuels via biological processes, optimization of chemical sequestration technologies, development of new environmental remediation strategies based on biostimulation approaches, and even the origin of life.

The microenvironment in the few cubic microns, at and adjacent to actively metabolizing cell surfaces can be significantly different from the bulk environment. Microbial polymers (polysaccharides, DNA, RNA, and proteins), whether attached to or

released from the cell, contribute to the development of steep chemical gradients over very short distances. It is currently difficult to understand the behavior of contaminant radionuclides and metals in such microenvironments. Thus, information about biotransformations and biogeochemical interactions at the microbe-mineral interface is crucial for predicting the fates of contaminants and designing effective bioremediation approaches.

There are numerous examples of the use of hard X-ray synchrotron radiation to investigate transformations of minerals, contaminant metals, and radionuclides, but only a small number of synchrotron-based microprobe studies have been performed to directly probe the microenvironment at and near the mineral-microbe interface. For example, X-ray microspectroscopy at the APS was recently used to describe a mechanism by which diatom-derived polyphosphates play a critical role in the formation of calcium phosphate minerals in marine sediments (Diaz, 2008). These results show how biogeochemical cycling of phosphorous is tied to that of carbon. Similarly, microspectroscopy has been applied to delineate the role of biofilms in chemically transforming carcinogenic heavy metals such as chromium (Kemner et al., 2004). Submicron x-ray microprobes have also been used to investigate the biological components of biogeochemical cycling. For instance, X-ray microprobe studies at the APS have identified mineral assemblages within microorganisms thought to facilitate respiration in the absence of an external oxidant (Glasauer et al., 2007), and biochemical mechanisms used by other microorganisms to scavenge reactive oxygen species (Daly et al., 2007).

Application of synchrotron technologies will enable the understanding of coupled biotic and abiotic processes under ambient and extreme environmental conditions, and will provide practical opportunities for scientific discoveries in environments contaminated with metals, radionuclides, and organics; agricultural sites to be used for the sustained production of biofuel feed stocks; degradation of cellulosic biofuel feedstocks; and systems affecting atmospheric CO<sub>2</sub> concentrations.

### Mineral physics and Earth and planetary interiors

Processes occurring within the interiors of Earth and other planets are controlled by the physical and chemical properties of the materials that compose these bodies. Most of what geologists and planetary scientists know about planetary interiors is based on seismic and gravity data, along with inferences from bulk composition and moment of inertia. Additional constraints on the structure, phase relations, and mechanical behavior of planetary interiors can be obtained directly from experimental studies of appropriate compositions performed at extreme conditions of pressure and temperature. These experiments can now be performed using pressurized devices such as the diamond anvil cell and the multi-anvil apparatus in which samples can be laser-heated under pressure, and measurements can be made *in situ* using ultrasonic methods, light scattering, and synchrotron radiation techniques including X-ray diffraction, X-ray inelastic scattering and X-ray absorption spectroscopy.

High-pressure experimentation in a laser-heated diamond anvil cell using highbrilliance, hard X-ray synchrotron radiation for in situ structure determination by X-ray diffraction resulted in the recent discovery of a post-perovskite phase of MgSiO<sub>3</sub> at conditions approximating those of the core-mantle boundary (Murakami et al., 2004). This discovery has major implications for the interpretation of the D" seismic discontinuity (Hirose, 2006), which has been a controversial geophysical topic for This example illustrates how such experimental data can constrain interpretations for seismic observations of density stratification in Earth and other planets. The composition and properties of Earth's core have fundamental implications for its geochemical evolution and dynamics, including the origin of Earth's magnetic field. Studies of the melting of candidate materials for the core (e.g., Fe and Ni, alloyed with light elements such as Si or S) as well as the physical properties of these molten fluids are needed to unravel the current composition and history of the core. Such studies should also be conducted with both static and dynamic compression techniques to achieve the extreme pressures of the extra-solar planets and provide time-resolved data. Finally, the advanced micro-analytical methods developed for high-pressure techniques can be used to study natural samples (Sobelev et al. 2000; Chen et al. 2003).

Some of the outstanding questions of geological and planetary science that can be addressed using synchrotron radiation are outlined in the workshop reports *Current and Future Research Directions in High-Pressure Mineral Physics* (Bass, 2004) and *Role of User Facilities in Earth Sciences Research* (Brown et al., 2006): How much potassium and other radioactive elements can be present in the core? What light elements are present in the core? What is the energy source that drives the geomagnetic dynamo? How does the core melting temperature vary with composition? What is the nature of the D" layer at the base of the mantle? Is the mantle partially molten at the core-mantle boundary? What is the crystal structure of the inner core, and is it partly molten? How do small amounts of water affect the properties of minerals at mantle conditions? What is the structure and behavior of hydrogen-rich compositions at temperatures and pressures characteristic of the outer planets and their icy satellites?

Over the past decade, special facilities have been developed and installed on beamlines at the APS to enable the next-generation state-of-the-art experiments in high-pressure earth and planetary science mineral physics to be performed. These include the diamond-anvil and multi-anvil apparatus at the GSECARS beamlines 13-BM and -ID, the high-pressurediamond-anvil facilities at HP-CAT and the nuclear resonant inelastic X-ray scattering facilities at XOR-3-ID. HPSynC is a consortium that supports the integration and development of high-pressure activities of some dozen beamlines at the APS involved in this area of research, including high-pressure geoscience. At each of these beamlines, new techniques are being added to this arsenal of tools to study the structure and behavior of materials at extreme conditions. Of critical importance is the need to integrate and exploit multiple techniques that take advantage of the unique features of different beamlines to understand high-pressure phenomena (e.g., Ding et al. 2008).

Ever brighter sources from 1-100 keV are essential for this work because photons remain the key probe of the crystallographic, electronic, and defect structures of minerals

and mineral assemblages under the most extreme conditions. There are important opportunities for exploring the nanophase materials described above to extreme conditions using <10 nm beams. New microfocusing/imaging techniques developed at the APS are opening up new fields for imaging complex natural assemblages, textured materials, and buried interfaces under extreme conditions (Hemley et al., 2005; Ice et al. 2005). Current single-phase diffraction/scattering techniques need to be extended to tomographic diffraction / spectroscopic (e.g., x-ray Raman; e.g., Hemley et al., 2007) imaging of bulk materials under extreme conditions using these nanometer-scale x-ray beams. In addition, there are plans for dedicated facilities for direct measurements of materials on dynamic compression, based on successful shock-wave single crystal x-ray measurements carried out at HPCAT in 2007 (Turneaure et al. 2008). As mentioned above, this new class of experiments, including combined static and dynamic compression measurements at synchrotron sources, hold the promise of accessing and probing entirely new P-T regimes within the Earth and other planets. The scientific questions listed above, and many others, can be addressed more effectively by improvements in the flux, brilliance, X-ray optics and detectors at APS.

# Cosmochemistry and Planetary Geochemistry

Clues to the origin and evolution of our Solar System and other cosmological bodies are locked within extraterrestrial materials available for laboratory study including lunar samples returned by the Apollo program; meteorites from the Moon, Mars and asteroids collected from Earth's surface, notably Antarctica; interplanetary dust particles collected in the stratosphere; comet particles collected by the Stardust spacecraft; and solar wind collected by the Genesis spacecraft. The science drivers involve fundamental questions: How did the universe begin and what is its ultimate fate? How did the Sun's family of planets and minor bodies originated and evolve to their present state? How did life begin on Earth and are conditions right for life on other bodies? What are the fundamental physical and chemical processes at work in the space environment from the Sun to Earth, to other planets, and beyond to the interstellar medium?

Synchrotron-based techniques are playing an important role in defining the states of these samples and obtaining insight into the properties of their parent bodies and the processes that formed them. Organics derived from individual (~10 micron) stratospheric interplanetary dust particles (IDPs), cometary dust, and meteorites are being studied by STXM and FTIR to test formation hypotheses such as catalytic reactions on mineral surfaces and provide insight into the likelihood of seeding of the earth by extraterrestrial material at the onset of terrestrial life (Flynn et al. 2003, Flynn et al. 2002, Messenger et al. 2000, Keller et al. 2004). New classes of extraterrestrial organic matter can also be discovered in this way (Sandford et al. 2006). Evidence for a close relationship between the dust in comets and carbonaceous meteorites is being provided by x-ray microprobe (XRM) compositional analyses (Flynn et al. 2006; Lanzirotti et al. 2008). The evolutionary relationships between primitive components of carbonaceous meteorites, such as chondrules and refractory inclusions, are being uncovered by microXAFS analyses (Simon et al. 2007ab, 2008). Formational environments of presolar SiC grains from meteorites are being revealed by XRM analyses (Kashiv 2004; Kashiv et al. 2002,

2006; Knight et al. 2008) and coupled RIMS analyses will eventually yield insight into the associated stellar types. Oxidation states of Martian siliceous melts are being determined by XRM analyses of Martian meteorites (Walton et al. 2008, Sutton et al. 2008) as well as the evolution of Martian fluids in its early history (Rao et al. 2005, 2008). Synchrotron-based x-ray standing wave methods offer one of the few opportunities to extract compositional data from the compromised Genesis solar wind collectors (Kitts et al. 2006, 2008). Synchrotron x-ray microdiffraction reveal new minerals and the origin of weathering on airless bodies such as the moon (Anand et al. 2004), as well as effects of shock metamorphism on planetary surfaces (Chen et al. 2003). Instrumentation at the APS is playing a vital role in the high energy components of this research.

This cutting edge, synchrotron-based, cosmochemical research is currently limited by spatial resolution and sensitivity capabilities. Extraterrestrial materials are exceedingly fine-grained (nm-scale) and synchrotron instrumentation is just beginning to be able to probe these materials at spatial scales where individual phases dominate. In addition, high elemental sensitivity in these sub-micrometer regions is essential. Elements of interest tend to be in trace concentrations indicating that analytical capabilities in the attogram range are required. Technical improvements that will drive these advances include higher brightness sources, improved optics (especially those capable of high efficiency and sub-micrometer beam production), improved detectors (primarily in terms of higher throughput but high energy resolution is also essential) and sample manipulation systems with higher spatial resolution and stability.

Accessibility is also a critical issue. The APS instruments currently used for this research are highly oversubscribed making it challenging to obtain comprehensive datasets in reasonable time periods. This accessibility shortfall can be addressed with the addition of new instruments, increase in the amount of beam time available on existing instruments, or a combination of these two approaches. Canted undulator upgrades are effective means for dramatically increasing instrument availability.

These technical advances will not only maximize our ability to extract information from currently available extraterrestrial material collections but also samples from future return missions, such as those likely to sample the Moon, Mars, asteroids and comets. The relatively non-destructive nature of the synchrotron x-ray analyses is extremely advantageous for characterization of these precious returned extraterrestrial materials that often are in exceedingly small quantities. The total comet dust collection returned by the Stardust spacecraft has an estimated mass of  $\sim 1$  mg. The total mass of the Genesis solar wind collection is estimated to be  $\sim 400~\mu g$ . Importantly, x-ray analyses can be done without sample alteration, often while within the collection substrates and containers, leaving the materials available for further destructive analyses that require extraction, such as isotopic composition by mass spectrometry. Such consortium-style analytical approaches maximize the science return from individual samples.

#### 4. References

- Anand, M. L., A. Taylor, M. A. Nazarov, J. Shu, H. K. Mao and R. J. Hemley (2004). Space weathering on airless planetary bodies: clues from the lunar mineral hapkeite. *Proc. Nat. Acad. Sci.* **101**, 6847-6851.
- Banfield J. F., Navrotsky A., Eds. *Nanoparticles and the Environment* (Mineralogical Society of America, Washington, DC, 2001).
- Bedzyk M.J. and Cheng L., 2002. X-ray standing wave studies of minerals and mineral surfaces: Principles and applications. *Reviews in Mineralogy and Geochemistry* 49, 221-266.
- Binnig, G., Quate, C. F. and Gerber, C., 1986. Atomic force microscope. *Physical Review Letters* 56, 930-933.
- Brown G.E., Jr. and Sturchio N.C., 2002. An overview of synchrotron radiation applications in low-temperature geochemistry and environmental science. *Reviews in Mineralogy and Geochemistry* 49, 1-115.
- Brown, G. E., G. Calas and R. J. Hemley (2006), Role of user facilities in Earth sciences research. *Elements*, **2**, 23-30.
- Catalano J. G., Heald S. M., Zachara J. M., Brown G. E., Jr., 2004, Spectroscopic and diffraction study of uranium speciation in contaminated vadose zone sediments from the Hanford site, Washington State. *Environmental Science & Technology* 38, 2822-2828.
- Chen, M., J. Shu, H. K. Mao, X. Xie, and R. J. Hemley (2003), Natural occurrence and synthesis of two new post-spinel polymorphs of chromite, *Proc. Nat. Acad. Sci.*, **100**, 14651-14654.
- Cheng, L., Fenter, P., Nagy, K. L., Schlegel, M. L. and Sturchio, N. C., 2001. Molecular-scale density oscillations in water adjacent to a mica surface. *Physical Review Letters* 87, 156103.
- Cygan, R. T., Kubicki, J. D., Eds. 2001. Molecular Modeling Theory: Applications in the Geosciences. *Reviews in Mineralogy and Geochemistry* 42, 531 pp.
- Daly M.J., E. K. Gaidamakova, V. Y. Matrosova, A. Vasilenko, M. Zhai, K. M. Kemner, B. Lai, B. Ravel, L. P. Wackett, S. W. Li, J. K. Fredrickson, "Protein Oxidation Implicated as the Primary Determinant of Bacterial Radioresistance," *PLoS Biology* Vol. 5, No. 4, e92 doi:10.1371/journal.pbio.0050092.
- Diaz J, Ingall E, Benitez-Nelson C, Paterson D, de Jonge MD, McNulty I, Brandes J.A., 2008. *Science* **320**, 652-655.
- Ding, Y., D. Haskel, S. G. Ovchinnikov, Y.-C. Tseng, Y. S. Orlov, J. C. Lang, and H. K. Mao (2008), Novel pressure-induced magnetic transition in magnetite (Fe<sub>3</sub>O<sub>4</sub>). *Physical Review Letters* **100**, 045508.
- DOE, 2007, Basic Research Needs for Geosciences: Facilitating 21<sup>st</sup> Century Energy Systems. <a href="http://www.sc.doe.gov/bes/reports/files/GEO\_rpt.pdf">http://www.sc.doe.gov/bes/reports/files/GEO\_rpt.pdf</a>.
- DOE, 2008, *Basic Research Needs for Materials under Extreme Environments*. <a href="http://www.sc.doe.gov/bes/reports/files/MUEE\_rpt.pdf">http://www.sc.doe.gov/bes/reports/files/MUEE\_rpt.pdf</a>
- Fenter, P. A., 2002. X-ray reflectivity as a probe of mineral-fluid interfaces: A user guide. *Reviews in Mineralogy and Geochemistry* 49, 149-220.
- Flynn G. J., Keller L. P., Feser M., Wirick S., & Jacobsen, C. (2003) The Origin of Organic Matter in the Solar System: Evidence from the Interplanetary Dust Particles. Geochim. Cosmochim. Acta 67, 4791-4806
- Flynn, G. J., and 79 others (2006) Elemental compositions of comet 81P/Wild 2 samples collected by Stardust. *Science* 314 (5806): 1731-1735 Dec. 15 2006.
- Flynn, G. J., Keller, L. P., Jacobsen, C., & Wirick, S. (2002) FTIR and Carbon-XANES Examination of Organic Carbon in Tagish Lake: Evidence for a Moderately Volatile Organic Component. Lunar & Planetary Science XXXII, 1593.
- Geissbühler, P., Fenter, P., DiMasi, E., Srajer, G., Sorensen, L. B. and Sturchio, N. C., 2004. Three-dimensional structure of the calcite-water interface. *Surface Science* 573, 191-203.
- Glasauer S, S. Langley, M. Boyanov, B. Lai, K. M. Kemner, T. J. Beveridge, 2007. Mixed valence cytoplasmic iron granules are linked to anaerobic respiration. *Applied and Environmental Microbiology* **73**, 993-996.
- Green H. W., II and Burnley P. C., 1989, A new self-organizing mechanism for deep-focus earthquakes. *Nature* 341, 733-737.
- Hemley, R. J., H. K. Mao, and V. V. Struzhkin (2005), Synchrotron radiation and high pressure: new light on materials under extreme conditions, *J. Synch. Radiation*, **12**, 135-154.
- Hemley, R. J., V. V. Struzhkin, and R. E. Cohen (2007), Measuring high-pressure electronic and magnetic properties, in *Treatise on Geophysics* (ed. G. D. Price), 293-337 (Elsevier, Amsterdam).

- Hirose K., 2006. Postperovskite phase transition and its geophysical implications. *Reviews of Geophysics* 44, RG3001, doi:101029/2005RG000186.
- Hochella, M. F. and Banfield, J. F., 1995. Chemical weathering of silicates in nature: A microscopic perspective with theoretical considerations. *Reviews in Mineralogy* 31, 353-406.
- Ice, G. P. Dera, W. Liu, and H. K. Mao (2005) Adapting polychromatic x-ray microdiffraction techniques to high-pressure research: energy scan approach. *J. Synch. Rad.* **12**, 6-9-617.
- Kashiv, Y. (2004) Trace element abundances in single presolar SiC grains by synchrotron x-ray fluorescence, Ph.D., The University of Chicago.
- Kashiv, Y., A. M. Davis, Z. Cai, B. Lai, S. R. Sutton, R. S. Lewis, R. Gallino and R. N. Clayton (2006) Extinct <sup>93</sup>Zr in Single Presolar SiC Grains and Condensation from Zirconium Depleted Gas. Lunar and Planetary Science XXXVII, LPI, Lunar and Planetary Institute, 2464.
- Kashiv, Y., Z. Cai, B. Lai, S. R. Sutton, R. S. Lewis, A. M. Davis, R. N. Clayton, and M. J. Pellin (2002) Condensation of trace elements into presolar SiC stardust grains. Lunar Planet. Sci. XXXIII, 2056.
- Keller, L. P., Messenger S., Flynn G. J., Clemett S., Wirick S., & Jacobsen C. (2004) The nature of molecular cloud material in interplanetary dust. *Geochim. Cosmochim. Acta* 68, 2577-2589.
- Kemner K.M., S. D. Kelly, B. Lai, J. Maser, E. J. O'Loughlin, D. Sholto-Douglas, Z. Cai, M. A. Schneegurt, C. F. Kulpa, Jr., K. H. Nealson, 2004. Elemental and redox analysis of single bacterial cells by X-ray microbeam analysis. *Science* 306, 686-687.
- Kerisit, S. and Parker, S. C., 2004. Free energy of adsorption of water and calcium on the (104) calcite surface. *Chemical Communications*, 52-53.
- Kitts, K., S. Sutton, P. Eng, S. Ghose, D. Burnett (2006) Discrimination and Quantification of Contamination and Implanted Solar Wind in Genesis Collector Shards Using Grazing Incidence Synchrotron X-Ray Techniques: Initial Results. Lunar and Planetary Science XXXVII, LPI, Lunar and Planetary Institute, 1451.
- Kitts, K., Y. Choi, P. Eng, S. Sutton, S. Ghose, D. Burnett (2008) Discrimination and Quantification of Implanted Solar Wind in Genesis Collector Shards Using Grazing Incidence Synchrotron X-Ray Techniques: New Detector Initial Results. Lunar and Planetary Science XXXIX, Lunar and Planetary Institute, Houston, TX, 1296.
- Knight, K. B., S. R. Sutton, M. Newville, A. M. Davis, N. Dauphas, R. S. Lewis, S. Amari, I. M. Steele, M. R. Savina and M. J. Pellin. (2008) Trace Element Determinations in Presolar SiC Grains by Synchrotron X-Ray Fluorescence: Commencement of a Coordinated Multimethod Study. Lunar and Planetary Science XXXIX, Lunar and Planetary Institute, Houston, TX, 2135.
- Lanzirotti, A., S. R. Sutton, G. J. Flynn, M. Newville and W. Rao (2008) Chemical composition and heterogeneity of Wild 2 cometary particles determined by synchrotron x-ray fluorescence. *Meteoritics & Planetary Science* 43, 187-214.
- Manceau A., Nagy K. L., Marcus M. A., Lanson M., Geoffroy N., Jacquet T., Kirpichtchikova T., 2008, Formation of metallic copper nanoparticles at the soil-root interface. *Environmental Science and Technology* 42, 1766-1772.
- Manceau A., Marcus M. A., and Tamura N., 2002, Quantitative speciation of heavy metals in soils and sediments by synchrotron X-ray techniques. In Applications of Synchrotron Radiation in Low-Temperature Geochemistry and Environmental Science. P. Fenter and N.C. Sturchio, Eds. Reviews in Mineralogy and Geochemistry, Mineralogical Society of America, Washington, DC., Vol. 49, 341-428.
- Messenger, S. (2000) Identification of molecular cloud material in interplanetary dust particles. *Nature* 404, 968-971.
- Michel F. M., Ehm L., Antao S. M., Lee P. L., Chupas P. J., Liu G., Strongin D. R., Schoonen M. A. A., Phillips B. L., and Parise J. B., 2007, The structure of ferrihydrite, a nanocrystalline material. Science 316, 1726-1729.
- Moreau J. W., Weber P. K., Martin M. C., Gilbert B., Hutcheon I. D., Banfield J. F., 2008, Extracellular proteins limit the dispersal of biogenic nanoparticles. *Science* 316, 1600-1603.
- Murakami M., Hirose K., Kawamura K., Sata N., Ohishi Y., 2004. Post-perovskite phase transition in MgSiO<sub>3</sub>. *Science* 304, 855-858.
- Navrotsky A., Mazeina L., and Majzlan J., 2008, Size-driven structural and thermodynamic complexity in irons oxides. Science 319, 1635-1638.
- Ohnesorge, F. and Binnig, G., 1993. True atomic-resolution by atomic force microscopy through repulsive and attractive forces. *Science* 260, 1451-1456.

- Park, S. H. and Sposito, G., 2002. Structure of water adsorbed on a mica surface. *Physical Review Letters* 89, 085501.
- Rao, M. N., L. E. Nyquist, S. J. Wentworth, D. H. Garrison, J. Herrin and S.R. Sutton (2008) Martian Fluids based on Mobile Element Studies in Salt-assemblages from Martian Meteorites. *J. G. R.-Planets*, 113, E06002, doi:10.1029/2007JE002958.
- Rao, M. N., S. R. Sutton, D. S. McKay and G. Dreibus (2005) Clues to Martian Brines based on Halogens in Salts from Nakhlites and MER Samples. *JGR-Planets* Early Mars Special Issue, 110, doi:10.1029/2005JE002470.
- Sandford, S., and 54 others (2006) Organics captured from comet 81P/Wild 2 by the Stardust spacecraft. *Science* 314, 1720-1724.
- Shen, Y. R., 1994. Surfaces probed by nonlinear optics. Surface Science 300, 551-562.
- Simon, S. B., S. R. Sutton and L. Grossman (2007a) The Valence of Titanium in Refractory Forsterite. Lunar and Planetary Science XXXVIII, LPI, 1892.
- Simon, S., S. R. Sutton and L. Grossman (2007b) Valence of Titanium and Vanadium in Pyroxene in Refractory Inclusion Interiors and Rims. *Geochim. Cosmochim. Acta* 71, 3098-3118.
- Simon, S. B., S. R. Sutton and L. Grossman. (2008) Constraints on the Oxidation State of Chondrule Precursors from Titanium XANES Analysis of Semarkona Chondrules. Lunar and Planetary Science XXXIX, Lunar and Planetary Institute, Houston, TX, 1352.
- Sobolev, N. V., B. A. Fursenko, S. V. Goryainov, J. Shu, R. J. Hemley, H. K. Mao, F. R. Boyd (2000), Fossilized high pressure from the Earth's deep interior: the coesite-in-diamond barometer, *Proc. Nat. Acad. Sci.*, **97**, 11875-11879.
- Soderholm L., Skanthakumar S., Gorman-Lewis D., Jensen M. P., and Nagy K. L., 2008, Characterizing solution and solid-phase amorphous uranyl silicates. *Geochimica et Cosmochimica Acta* 72, 140-150.
- Sutton, S. R., M. N. Rao, and L. E. Nyquist. (2008) Sulfur and Iron Speciation in Gas-Rich Impact-Melt Glasses from Basaltic Shergottites Determined by MicroXANES. Lunar and Planetary Science XXXIX, Lunar and Planetary Institute, Houston, TX, 1961.
- Turneaure, S. J., Y. M. Gupta, K. Zimmerman, K. Perkins, C. S. Yoo, and G. Shen (2008), Real-time microstructure of shocked crystals using synchrotron x-rays, *Science*, submitted.
- Walton, E. L., P. Jugo, and C. D. K. Herd (2008) The nature and origin of localized shock melts in Martian meteorites: Major and trace element composition, sulfur speciation and texture of EET 79001 shock melt veins and pockets. Lunar and Planetary Science XXXIX, Lunar and Planetary Institute, Houston, TX, 1880.
- Wilson B., Dewers T., Reches Z., Brune J., 2005. Particle size and energetics of gouge from earthquake rupture zones. *Nature* 434, 749-752.