

**Beamline Status and Planning Summary Document**  
**APS Scientific Advisory Committee Review**

**GeoSoilEnviroCARS (Sector 13)**

**September 2018**

## **1. Overview**

### **1.1. Scientific Focus**

GeoSoilEnviroCARS (GSECARS) is a national user facility dedicated to frontier research in the earth, environmental and planetary sciences. The research conducted at this facility is advancing our knowledge of the composition, structure and properties of earth materials, the processes they control and the processes that produce them. Most principal synchrotron-based analytical techniques in demand by these scientists are available for use by the entire community: (1) high-pressure/high-temperature powder diffraction and spectroscopy using the diamond anvil cell (DAC); (2) high-pressure/high-temperature powder diffraction and imaging using the large-volume press; (3) micro X-ray absorption fine structure spectroscopy; (4) micro X-ray fluorescence and powder micro-diffraction mapping; (5) microtomography; (6) high-pressure/high-temperature single crystal diffraction in the DAC (7) high-pressure/high-temperature total scattering in the DAC and PE cell. (8) powder and interface diffraction.

### **1.2. Sector Status**

The sector consists of canted undulator beamlines (13ID), a split bending magnet beamline (13BM), and three support laboratories. Each beamline consists of a first optics enclosure (13ID-A and 13BM-A), second optics enclosure (13ID-B and 13BM-B), and experimental stations (13ID-C, 13ID-D, 13ID-E, 13BM-C, and 13BM-D). Four of the five experimental stations operate simultaneously: 13BM-C, 13BM-D, 13ID-E, and 13ID-C or 13ID-D. The primary instrumentation and techniques available in each station are summarized below:

#### Undulator Beamline (13ID)

- Station 13ID-A (1st Optical Enclosure): Primary beamline slits, two cryogenic Si (111 & 311) monochromators, diagnostic tanks, horizontal deflecting and focusing mirrors (13ID-E), white beam power limiting aperture. (13ID-C/D)
- Station 13ID-B (2nd Optical Enclosure): Vertical focusing mirror (13ID-C/D), secondary source aperture (13ID-E), diagnostic tank with BPM's for 13ID-E and 13ID-C/D, inboard and outboard branch safety shutters
- Station 13ID-C (1st Experimental Station): Horizontal focusing mirror (13ID-C/D), General Purpose Diffractometer (crystal truncation rod, X-ray standing waves, reflectivity, grazing incidence XRF, grazing incidence XAFS, inelastic X-ray scattering, microcrystallography)
- Station 13ID-D (2nd Experimental Station): Laser Heated Diamond Anvil Cell Diffractometer (angular dispersive micro-diffraction, emission spectroscopy); 1000-ton Multi-anvil Press (energy dispersive diffraction, angular dispersive diffraction, radiography)
- Station 13ID-E (3rd Experimental Station): X-ray Microprobe (microXRF, microXAFS, microXRD, fluorescence microtomography)

#### Bending Magnet Beamline (13BM)

- Station 13BM-A (1st Optical Enclosure): Primary beamline slits, water-cooled Si (111) monochromator (13BM-D)
- Station 13BM-B (2nd Optical Enclosure): Vertical focusing mirror (13BM-D), vertical focusing mirror (13BM-C); horizontal focusing Si (111 & 311) monochromator (13BM-C), shutters (13BM-D and 13BM-C)

- Station 13BM-C (Side Experimental Station): General Purpose Diffractometer (powder and single crystal diffraction in the DAC, crystal truncation rod, X-ray standing waves, reflectivity, powder diffraction, microcrystallography,)
- Station 13BM-D (End Experimental Station): Externally Heated Diamond Anvil Cell Diffractometer (angular dispersive micro-diffraction, Brillouin and Raman spectroscopy); Microtomography Apparatus (transmission and differential absorption computed microtomography); 250-ton Multi-anvil Press (energy dispersive diffraction, angular dispersive diffraction, radiography, high-pressure tomography)

### 1.3. Management Structure

GSECARS is part of the Center for Advanced Radiation Sources (CARS) at the University of Chicago. CARS (Mark Rivers, Executive Director) operates sectors 13, 14, and 15 at the APS. GSECARS management consists of Co-Project Managers: Mark Rivers and Stephen Sutton, and six Technical Groups organized around the six principal techniques in the sector. Each of these groups has a senior GSECARS staff member as a leader as shown below:

- Diamond Anvil Cell: Vitali Prakapenka (lead; Research Professor), Sergey Tkachev (Beamline Scientist)
- Large-Volume Press: Yanbin Wang (lead, Research Professor), Tony Yu (Beamline Scientist)
- Microtomography: Mark Rivers (lead, Research Professor)
- X-ray Absorption Fine Structure Spectroscopy: Matt Newville (lead, Research Associate Professor), Tony Lanzirotti (Research Associate Professor)
- X-ray Diffraction and Scattering: Peter Eng (lead, Research Professor), Joanne Stubbs (Research Associate Professor)
- X-ray Fluorescence Microprobe: Stephen Sutton (lead, Research Professor)

These individuals have the responsibility to lead the development of science, instrumentation and user community in their particular area. In addition, they work closely with users to ensure the success of experiments (experiment design, experiment conduct, data analysis, etc.) and receive input from them on potential new technical directions. This management configuration has worked successfully throughout the history of GSECARS.

In 2015, GSECARS formed a new partnership with the NSF-funded Consortium for Materials Properties Research in Earth Sciences (COMPRES). It is called the Partnership for Extreme Crystallography (PX2) and the Principal Investigator is Przemek Dera from the University of Hawaii. The goal is to develop and operate a user program for single-crystal and powder diffraction in the diamond anvil cell on the 13BM-C station. PX2 currently funds a full-time beamline scientist (Dongzhou Zhang) who is resident at GSECARS. There is currently a search in progress for a second scientist to assist Dongzhou. Prior to 2015, 13BM-C was used for interface science and ambient pressure powder diffraction, and was not fully subscribed. The introduction of the PX2 program has led to this beamline now being oversubscribed.

GSECARS has a second partnership with COMPRES to help operate the gas loading system at sector 13 for non-GSECARS users. This includes users at other APS beamlines (e.g. sectors 3, 16, 30, 34) and a mail-in program for users at other synchrotrons and home laboratories. COMPRES funds 50% of Sergey Tkachev under this partnership.

## 2. Scientific Focus

### 2.1. General Areas of Focus

A wide range of research is being undertaken covering topics including the chemistry, nature, and dynamics of Earth's core and mantle; processes at work in the Earth's crust that control the transport and

bio-availability of toxic species; and the evolution of our solar system revealed through the study of extraterrestrial materials. The majority of this research can be divided into the following categories:

***High Pressure Mineral Physics and Chemistry:*** The primary goal of high-pressure mineral physics research is to provide a laboratory basis for understanding the state and dynamics of the Earth's deep interior. Together, the diamond anvil cell (DAC) and large volume press (LVP) apparatus provide a powerful resource for studies of the structures and properties of minerals under the precise pressure and temperature conditions at all depths within the Earth. The GSECARS high pressure instrumentation is utilized for a wide range of experiments related to the composition of the Earth's mantle and core and the processes at work in the deep Earth including equations of state and phase relations, element partitioning, accurate structural determinations, elasticity, rheology, kinetics of phase transformations, and chemical reactions at extreme conditions.

***Non-crystalline and Nano-crystalline Materials at High Pressure:*** Critical for modeling processes of planetary differentiation is a detailed knowledge of the rheological properties of silicate melts and the melting properties of Earth materials at conditions reaching those in the deep mantle. The GSECARS LVPs allow direct measurement of melt viscosities at high pressures using real-time X-ray radiography to monitor the fall of dense marker spheres through molten silicate melt. Melting temperatures at high pressure can be inferred in the DAC through observations of diffuse scattering and the disappearance of crystalline diffraction peaks. Liquid and amorphous structure measurements are performed using the total scattering technique in both the DAC and a Paris-Edinburgh press using Soller slits and a new Pilatus 300K CdTe detector. The grain size dependence of phase transitions in nano-crystalline materials can also be investigated in the DAC.

***Chemistry of Magmas and their associated Hydrothermal Fluids:*** Microfocused X-ray absorption fine structure techniques allow for direct measurement of the speciation of redox sensitive elements (eg. Fe, V, Cr, Eu, Ti, S, etc.) in magmatic minerals and glasses. Since oxygen fugacity ( $fO_2$ ) plays a vital role in determining the stability and composition of crystallizing phases, the oxidation state of multivalent elements, and the composition and stability of fluid and volatile phases in a magma, such direct measurement of elemental speciation and valence allows researchers to then quantitatively constrain the redox conditions for magmas derived by the melting of planetary mantles. This is critical to our understanding of the genesis and differentiation of magmas, associated ore deposits and for modeling the evolution of planetary interiors. These XAFS methods are also applied in studying the hydrothermal fluids associated with magmatic systems. Hot fluids within the Earth are important conduits for chemical transport. For example, ore-deposits such as porphyry Cu and epithermal Au(Cu) form from metals transported as complex ions in hydrothermal solutions. To understand the formation of these deposits, it is necessary to determine the metal complexes, and their stability, as a function of variables such as temperature and fluid composition. The GSECARS microprobe is well-suited for such studies using X-ray absorption spectroscopic techniques on individual fluid inclusions, both natural and synthetic.

***Reactions at Mineral-Water Interfaces:*** Chemical interactions at interfaces between solids and aqueous solutions often dominate the fate and transport of trace elements and pollutants within the Earth's hydrosphere and are largely responsible for the trace element composition of the oceans. As such, the overall composition and speciation of an aquatic system are strongly influenced by processes such as: (i) the adsorption of dissolved species on the surfaces of mineral phases (including nanoparticles), fine-grained amorphous materials, organic and microbial materials, and inorganic and/or organic films coating mineral surfaces; (ii) the incorporation of dissolved species within phases precipitated from solution; (iii) release of chemical species to solution through dissolution or desorption; and (iv) mobilization or flocculation of nanoparticles. The development of a fundamental understanding of these processes requires detailed experimental studies of the structure, composition, and chemical mechanisms at solid-aqueous solution interfaces. A number of complementary surface-sensitive techniques are currently in place at GSECARS including; (1) crystal truncation rod diffraction and grazing-angle reflectivity for the analysis of surface and interface structure; (2) X-ray absorption fine structure and grazing-incidence absorption spectroscopy to probe the local structure and oxidation state of surface-bound species; and (3) X-ray standing wave fluorescence-yield measurements for the determination of the position and distribution of surface and

interfacial species. The GSECARS General Purpose Diffractometers allow a combination of these techniques to be applied on samples under *in situ* conditions (i.e., in the presence of bulk solution or controlled atmosphere).

**Biogeochemistry:** Improving the accuracy of contaminant transport models is one of the biggest challenges facing environmental geochemists. Bacteria are ubiquitous in surface waters and in the subsurface, even to depths of several kilometers. These microbes have an extremely high affinity to adsorb aqueous metal cations, and the ability to mediate redox reactions, potentially dominating the speciation of the metals in the environment. An important aspect of the research at GSECARS is to improve our understanding of the molecular-scale processes that control contaminant-microbe adsorption and redox reactions, and the effect of these processes on contaminant transport. The GSECARS microprobe provides instrumentation to biogeochemists for measuring redox mediated changes in chemistry (from the S K-edge through to the Cd K-edge) at appropriate length scales, both in natural samples and within environmentally-controlled experimental cells.

**Flow Dynamics of Fluids and Solids:** Many processes in the earth's surface are controlled by the microscale interaction of water and air with the solid phase (soils, sediments, rock) in pore spaces within the subsurface. The distribution in time and space of fluids in pores ultimately controls subsurface flow and transport processes relevant to groundwater resource management and remediation as well as oil and gas exploration and recovery. Many of the mechanisms operating at the microscale can be observed through the measurement of relevant physical parameters (e.g. fluid phase content and distribution, pore size distribution, permeability, porosity) using computed microtomography. In addition, the flow of solids is important in understanding earthquake propagation.

**Cosmochemical Studies of Extraterrestrial Materials:** 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; interplanetary dust particles collected in the stratosphere; comet particles collected by the Stardust spacecraft; and solar wind collected by the Genesis spacecraft. Synchrotron-based techniques, primarily X-ray microprobe, tomography, microXAFS and X-ray standing waves, allow us to define the chemical states of these samples and obtain insight into the properties of their parent bodies.

## 2.2. Science Highlights

Here we provide brief summaries of science highlights for each of the five experimental stations.

### Beamline 13-ID-C

#### **Response of Interfacial Water to Arsenate Adsorption on Corundum (001) Surfaces: Effects of pH and Adsorbate Surface Coverage**

Publication: Tingying Xu, Joanne E. Stubbs, Peter J. Eng, Jeffery G. Catalano (2018) **Geochim. Cosmochim. Acta** 239, 198-212. DOI: 10.1016/j.gca.2018.07.041

The interaction of water with metal oxide mineral surfaces affects chemical reactions that are important to many natural processes. Previous studies demonstrate that the various functional groups on mineral surfaces control ion adsorption as well as the ordering of interfacial water, but the effect of water structure on the reactivity and dynamics of interfacial reactions has not been systematically investigated. In this study, surface X-ray scattering measurements on corundum (0 0 1) surfaces with and without arsenate over a range of pH conditions have been used to determine the response of interfacial water structure to arsenate adsorption. In the absence of arsenate, the structure of interfacial water near this surface varies little over the pH range of 5–9, suggesting that surface charging from protonation-deprotonation under the conditions studied is inadequate to induce extensive restructuring. In contrast, interfacial water undergoes substantial restructuring upon arsenate adsorption, indicating that charged surface complexes substantially perturb the arrangement and order of interfacial water on this surface. The overall interfacial water structure also varies proportionally with arsenate surface coverage, with adsorbed water layers moving closer to the surface and the extended layering of interfacial water showing reduced positional disorder as arsenate surface coverage increases. Systematic variations in interfacial water properties with increasing arsenate concentration at each pH value are consistent with the coexistence of two distinct water structures (in the absence and presence of adsorbed arsenate) that vary in proportion with adsorbate surface coverage. These observations demonstrate that the adsorption of arsenate alters the structure of interfacial water near corundum (0 0 1) surfaces, possibly through the modification of the charge state of surface sites or by providing new sites to which water may hydrogen bond. Such adsorbate-induced restructuring of interfacial water may contribute to the energetics of chemical reactions at mineral-water interfaces.

#### **Oxidative Corrosion of the UO<sub>2</sub> (001) Surface by Nonclassical Diffusion**

Publication: Joanne E. Stubbs, Craig A. Biwer, Anne M. Chaka, Eugene S. Ilton, Yingge Du, John R. Bargar, Peter J. Eng (2017), **Langmuir** 33 (46), 13189-13196. DOI: 10.1021/acs.langmuir.7b02800

Uranium oxide is central to every stage of the nuclear fuel cycle, from mining through fuel fabrication and use, to waste disposal and environmental cleanup. Its chemical and mechanical stability are intricately linked to the concentration of interstitial O atoms within the structure and the oxidation state of U. We have previously shown that, during corrosion of the UO<sub>2</sub> (111) surface under either 1 atm of O<sub>2</sub> gas or oxygenated water at room temperature, oxygen interstitials diffuse into the substrate to form a superlattice with three-layer periodicity. In the current study, we used surface X-ray scattering to reveal the structure of the oxygen diffusion profile beneath the (001) surface. The first few layers below the surface oscillate strongly in their surface-normal lattice parameters, suggesting preferential interstitial occupation of every other layer below the surface, which is geometrically consistent with the interstitial network that forms below the oxidized (111) surface. Deeper layers are heavily contracted and indicate that the oxidation front penetrates ~52 Å below the (001) surface after 21 days of dry O<sub>2</sub> gas exposure at ambient pressure and temperature. X-ray photoelectron spectroscopy indicates U is present as U(IV), U(V), and U(VI).

#### **Dynamic Stabilization of Metal Oxide–Water Interfaces**

Publication: Martin E. McBriarty, Guido Falk von Rudorff, Joanne E. Stubbs, Peter J. Eng, Jochen Blumberger, Kevin M. Rosso (2017), **J. Am. Chem. Soc.** 139 (7), 2581-2584. DOI: 10.1021/jacs.6b13096

The interaction of water with metal oxide surfaces plays a crucial role in the catalytic and geochemical behavior of metal oxides. In a vast majority of studies, the interfacial structure is assumed to arise from a

relatively static lowest energy configuration of atoms, even at room temperature. Using hematite ( $\alpha\text{-Fe}_2\text{O}_3$ ) as a model oxide, we show through a direct comparison of in situ synchrotron X-ray scattering with density functional theory-based molecular dynamics simulations that the structure of the (1 $\bar{1}$ 02) termination is dynamically stabilized by picosecond water exchange. Simulations show frequent exchanges between terminal aquo groups and adsorbed water in locations and with partial residence times consistent with experimentally determined atomic sites and fractional occupancies. Frequent water exchange occurs even for an ultrathin adsorbed water film persisting on the surface under a dry atmosphere. The resulting time-averaged interfacial structure consists of a ridged lateral arrangement of adsorbed water molecules hydrogen bonded to terminal aquo groups. Surface  $\text{pK}_a$  prediction based on bond valence analysis suggests that water exchange will influence the proton-transfer reactions underlying the acid/base reactivity at the interface. Our findings provide important new insights for understanding complex interfacial chemical processes at metal oxide–water interfaces. .

**Discrimination and Quantification of Fe and Ni abundances in Genesis Solar Wind Implanted Collectors using X-ray Standing Wave Fluorescence Yield Depth Profiling with Internal Referencing**  
Publication: Y. Choi, P. Eng, J. Stubbs, S.R. Sutton, M. Schmeling, I.V. Veryovkin, D. Burnett (2016)  
**Chem. Geol.** 441, 246-255. DOI: 10.1016/j.chemgeo.2016.08.025

X-ray standing wave fluorescence yield depth profiling was used to determine the solar wind implanted Fe and Ni fluences in a silicon-on-sapphire (SoS) Genesis collector (60326). An internal reference standardization method was developed based on fluorescence from Si and Al in the collector materials. Measured Fe fluence agreed well with that measured previously by us on a sapphire collector (50722) as well as SIMS results by Jurewicz et al. Measured Ni fluence was higher than expected by a factor of two; neither instrumental errors nor solar wind fractionation effects are considered significant perturbations to this value. Impurity Ni within the epitaxial Si layer, if present, could explain the high Ni fluences and therefore needs further investigation. As they stand, these results are consistent with minor temporally-variable Fe and Ni fractionation on the timescale of a year.

## Beamline 13-ID-D

### Ice-VII Inclusions in Diamonds: Evidence for Aqueous Fluid in Earth's Deep Mantle

Publication: O. Tschauner, S. Huang, E. Greenberg, V.B. Prakapenka, C. Ma, G.R. Rossman, A.H. Shen, D. Zhang, M. Newville, A. Lanzirotti, K. Tait (2018) *Science* 359 (6380), 1136-1139. DOI: 10.1126/science.aao3030

Water-rich regions in Earth's deeper mantle are suspected to play a key role in the global water budget and the mobility of heat-generating elements. We show that ice-VII occurs as inclusions in natural diamond and serves as an indicator for such water-rich regions. Ice-VII, the residue of aqueous fluid present during growth of diamond, crystallizes upon ascent of the host diamonds but remains at pressures as high as 24 gigapascals; it is now recognized as a mineral by the International Mineralogical Association. In particular, ice-VII in diamonds points toward fluid-rich locations in the upper transition zone and around the 660-kilometer boundary.

### Seismic Anisotropy of the D'' Layer Induced by (001) Deformation of Post-Perovskite

Publication: Xiang Wu, Jung-Fu Lin, Pamela Kaercher, Zhu Mao, Jin Liu, Hans-Rudolf Wenk, Vitali B. Prakapenka (2017), *Nat. Commun.* 8, 14669-1-14669-6. DOI: 10.1038/ncomms14669

Crystallographic preferred orientation (CPO) of post-perovskite (Mg,Fe)SiO<sub>3</sub> (pPv) has been believed to be one potential source of the seismic anisotropic layer at the bottom of the lower mantle (D'' layer). However, the natural CPO of pPv remains ambiguous in the D'' layer. Here we have carried out the deformation experiments of pPv-(Mg<sub>0.75</sub>,Fe<sub>0.25</sub>)SiO<sub>3</sub> using synchrotron radial X-ray diffraction in a membrane-driven laser-heated diamond anvil cell from 135 GPa and 2,500 K to 154 GPa and 3,000 K. Our results show that the intrinsic texture of pPv-(Mg<sub>0.75</sub>,Fe<sub>0.25</sub>)SiO<sub>3</sub> should be (001) at realistic P–T conditions of the D'' layer, which can produce a shear wave splitting anisotropy of ~3.7% with  $V_{SH} > V_{SV}$ . Considering the combined effect of both pPv and ferropericlase, we suggest that 50% or less of deformation is sufficient to explain the origin of the shear wave anisotropy observed seismically in the D'' layer beneath the circum-Pacific rim.

### Synthesis of Sodium Polyhydrides at High Pressures

Victor V. Struzhkin, Duck Young Kim, Elissaios Stavrou, Takaki Muramatsu, Ho-Kwang Mao, Chris J. Pickard, Richard J. Needs, Vitali B. Prakapenka, Alexander F. Goncharov, *Nat. Commun.* 7, 12267-1-12267-8 (2016). DOI: 10.1038/ncomms12267

The only known compound of sodium and hydrogen is archetypal ionic NaH. Application of high pressure is known to promote states with higher atomic coordination, but extensive searches for polyhydrides with unusual stoichiometry have had only limited success in spite of several theoretical predictions. Here we report the first observation of the formation of polyhydrides of Na (NaH<sub>3</sub> and NaH<sub>7</sub>) above 40 GPa and 2,000 K. We combine synchrotron X-ray diffraction and Raman spectroscopy in a laser-heated diamond anvil cell and theoretical random structure searching, which both agree on the stable structures and compositions. Our results support the formation of multicenter bonding in a material with unusual stoichiometry. These results are applicable to the design of new energetic solids and high-temperature superconductors based on hydrogen-rich materials.

### Terapascal Static Pressure Generation with Ultrahigh Yield Strength Nanodiamond

Natalia Dubrovinskaia, Leonid Dubrovinsky, Natalia A. Solopova, Artem Abakumov, Stuarat Turner, Michael Hanfland, Elena Bykova, Maxim Bykov, Clemens Prescher, Vitali B. Prakapenka, Sylvain Petitgirard, Irina Chuvashova, Bilianna Gasharova, Yves-Laurent Mathis, Petr Ershov, Irina Snigireva, Anatoly Snigirev, *Sci. Advances* 2 (7), e1600341-1-e1600341-12 (2016). DOI: 10.1126/sciadv.1600341

Studies of materials' properties at high and ultrahigh pressures lead to discoveries of unique physical and chemical phenomena and a deeper understanding of matter. In high-pressure research, an achievable static pressure limit is imposed by the strength of available strong materials and design of high-pressure devices. Using a high-pressure and high-temperature technique, we synthesized optically transparent microballs of bulk nanocrystalline diamond, which were found to have an exceptional yield strength (~460

GPa at a confining pressure of ~70 GPa) due to the unique microstructure of bulk nanocrystalline diamond. We used the nanodiamond balls in a double-stage diamond anvil cell high-pressure device that allowed us to generate static pressures beyond 1 TPa, as demonstrated by synchrotron x-ray diffraction. Outstanding mechanical properties (strain-dependent elasticity, very high hardness, and unprecedented yield strength) make the nanodiamond balls a unique device for ultrahigh static pressure generation. Structurally isotropic, homogeneous, and made of a low-Z material, they are promising in the field of x-ray optical applications.

### **Carbonate Stability in the Reduced Lower Mantle**

Publication: Susannah M. Dorfman, James Badro, Farjam Nabiei, Vitali B. Prakapenka, Marco Cantoni, Philippe Gillet (2018) **Earth Planet. Sci. Lett.** 489, 84-91. DOI: 10.1016/j.epsl.2018.02.035

Carbonate minerals are important hosts of carbon in the crust and mantle with a key role in the transport and storage of carbon in Earth's deep interior over the history of the planet. Whether subducted carbonates efficiently melt and break down due to interactions with reduced phases, or are preserved to great depths and ultimately reach the core-mantle boundary, remains controversial. In this study, experiments in the laser-heated diamond anvil cell (LHDAC) on layered samples of dolomite (Mg, Ca)CO<sub>3</sub> and iron at pressure and temperature conditions reaching those of the deep lower mantle show that carbon-iron redox interactions destabilize the MgCO<sub>3</sub> component, producing a mixture of diamond, Fe<sub>7</sub>C<sub>3</sub>, and (Mg, Fe)O. However, CaCO<sub>3</sub> is preserved, supporting its relative stability in carbonate-rich lithologies under reducing lower mantle conditions. These results constrain the thermodynamic stability of redox-driven breakdown of carbonates and demonstrate progress towards multiphase mantle petrology in the LHDAC at conditions of the lowermost mantle.

### **Early Episodes of High-pressure Core Formation Preserved in Plume Mantle**

Publication: Colin R.M. Jackson, Neil R. Bennett, Zhixue Du, Elizabeth Cottrell, Yingwei Fei (2018) **Nature** 553, 491-495. DOI: 10.1038/nature25446

The decay of short-lived iodine (I) and plutonium (Pu) results in xenon (Xe) isotopic anomalies in the mantle that record Earth's earliest stages of formation. Xe isotopic anomalies have been linked to degassing during accretion, but degassing alone cannot account for the co-occurrence of Xe and tungsten (W) isotopic heterogeneity in plume-derived basalts and their long-term preservation in the mantle. Measurements of I partitioning between liquid Fe alloys and liquid silicates at high pressure and temperature suggest that Xe isotopic anomalies found in modern plume rocks (that is, rocks with elevated <sup>3</sup>He/<sup>4</sup>He ratios) result from I/Pu fractionations during early, high-pressure episodes of core formation. Our measurements demonstrate that I becomes progressively more siderophile as pressure increases, so that portions of mantle that experienced high-pressure core formation will have large I/Pu depletions not related to volatility. These portions of mantle could be the source of Xe and W anomalies observed in modern plume-derived basalts. Portions of mantle involved in early high-pressure core formation would also be rich in FeO, and hence denser than ambient mantle. This would aid the long-term preservation of these mantle portions, and potentially points to their modern manifestation within seismically slow, deep mantle reservoirs with high <sup>3</sup>He/<sup>4</sup>He ratios.

### **High Poisson's Ratio of Earth's Inner Core Explained by Carbon Alloying**

Publication: C. Prescher, L. Dubrovinsky, E. Bykova, I. Kupenko, K. Glazyrin, A. Kantor, C. McCammon, M. Mookherjee, Y. Nakajima, N. Miyajima, R. Sinmyo, V. Cerantola, N. Dubrovinskaia, V. Prakapenka, R. Rüffer, A. Chumakov, M. Hanfland (2015), **Nat. Geoscience** 8, 220-223. DOI: 10.1038/ngeo2370

Geochemical, cosmochemical, geophysical, and mineral physics data suggest that iron (or iron–nickel alloy) is the main component of the Earth's core. The inconsistency between the density of pure iron at pressure and temperature conditions of the Earth's core and seismological observations can be explained by the presence of light elements. However, the low shear wave velocity and high Poisson's ratio of the Earth's core remain enigmatic. We experimentally investigated the effect of carbon on the elastic properties of iron at high pressures and temperatures and observe a high-pressure orthorhombic phase of iron carbide, Fe<sub>7</sub>C<sub>3</sub>. We determined the crystal structure of the material at ambient conditions and investigated its stability

and behaviour at pressures up to 205 GPa and temperatures above 3,700 K using single-crystal and powder X-ray diffraction, Mössbauer spectroscopy, and nuclear inelastic scattering. Estimated shear wave and compressional wave velocities show that  $\text{Fe}_7\text{C}_3$  exhibits a lower shear wave velocity than pure iron and a Poisson's ratio similar to that of the Earth's inner core. We suggest that carbon alloying significantly modifies the properties of iron at extreme conditions to approach the elastic behaviour of rubber. Thus, the presence of carbon may explain the anomalous elastic properties of the Earth's core.

### **Experimental Evidence Supports Mantle Partial Melting in the Asthenosphere**

Publication: Julien Chantle, Geeth Manthilake, Denis Andrault, Davide Novella, Tony Yu, Yanbin Wang (2016) *Sci. Advances* 2 (5), e1600246-1-e1600246-7. DOI: 10.1126/sciadv.1600246

The low-velocity zone (LVZ) is a persistent seismic feature in a broad range of geological contexts. It coincides in depth with the asthenosphere, a mantle region of lowered viscosity that may be essential to enabling plate motions. The LVZ has been proposed to originate from either partial melting or a change in the rheological properties of solid mantle minerals. The two scenarios imply drastically distinct physical and geochemical states, leading to fundamentally different conclusions on the dynamics of plate tectonics. We conducted in situ ultrasonic velocity measurements on a series of partially molten samples, composed of mixtures of olivine plus 0.1 to 4.0 volume % of basalt, under conditions relevant to the LVZ. Our measurements provide direct compressional ( $V_P$ ) and shear ( $V_S$ ) wave velocities and constrain attenuation as a function of melt fraction. Mantle partial melting appears to be a viable origin for the LVZ, for melt fractions as low as ~0.2%. In contrast, the presence of volatile elements appears necessary to explain the extremely high  $V_P/V_S$  values observed in some local areas. The presence of melt in LVZ could play a major role in the dynamics of plate tectonics, favoring the decoupling of the plate relative to the asthenosphere.

## Beamline 13-ID-E

### **Redox Variations in Mauna Kea Lavas, the Oxygen Fugacity of the Hawaiian Plume, and the Role of Volcanic Gases in Earth's Oxygenation**

Publication: Maryjo Brounce, Edward Stolper, John Eiler (2017) *Proc. Natl. Acad. Sci. USA* 114 (34), 8997-9002. DOI: 10.1073/pnas.1619527114

The behavior of C, H, and S in the solid Earth depends on their oxidation states, which are related to oxygen fugacity ( $fO_2$ ). Volcanic degassing is a source of these elements to Earth's surface; therefore, variations in mantle  $fO_2$  may influence the  $fO_2$  at Earth's surface. However, degassing can impact magmatic  $fO_2$  before or during eruption, potentially obscuring relationships between the  $fO_2$  of the solid Earth and of emitted gases and their impact on surface  $fO_2$ . We show that low-pressure degassing resulted in reduction of the  $fO_2$  of Mauna Kea magmas by more than an order of magnitude. The least degassed magmas from Mauna Kea are more oxidized than midocean ridge basalt (MORB) magmas, suggesting that the upper mantle sources of Hawaiian magmas have higher  $fO_2$  than MORB sources. One explanation for this difference is recycling of material from the oxidized surface to the deep mantle, which is then returned to the surface as a component of buoyant plumes. It has been proposed that a decreasing pressure of volcanic eruptions led to the oxygenation of the atmosphere. Extension of our findings via modeling of degassing trends suggests that a decrease in eruption pressure would not produce this effect. If degassing of basalts were responsible for the rise in oxygen, it requires that Archean magmas had at least two orders of magnitude lower  $fO_2$  than modern magmas. Estimates of  $fO_2$  of Archean magmas are not this low, arguing for alternative explanations for the oxygenation of the atmosphere.

### **Vanadium, Sulfur, and Iron Valences in Melt Inclusions as a Window into Magmatic Processes: A Case Study at Nyamuragira Volcano**

Publication: Elisabet Head, Antonio Lanzirrotti, Matthew Newville, Stephen Sutton (2018). *Geochim. Cosmochim. Acta* 226, 149-173. DOI: 10.1016/j.gca.2018.01.033

This study describes microscale sulfur (S), vanadium (V), and iron (Fe) K-edge X-ray absorption near edge structure ( $\mu$ -XANES) spectroscopy measurements on olivine-hosted melt inclusions (MI) preserved in tephra (1986 and 2006) and lavas (1938 and 1948) erupted from Nyamuragira volcano (D.R. Congo, Africa). The S, V, and Fe spectroscopic data are used to constrain the evolution of oxygen fugacity ( $fO_2$ ) and sulfur speciation for the entrapped melts. Melt inclusions from lavas show evidence of post-entrapment crystallization and were thus reheated prior to  $\mu$ -XANES analysis. The MI from tephra show no evidence of post-entrapment crystallization and were, therefore, not reheated. Sulfur, V, and Fe  $\mu$ -XANES results from 1938, 1948, and 2006 eruptive materials are all similar within analytical uncertainty and provide similar average calculated melt  $fO_2$ 's based on XANES oxybarometry. However, olivine-hosted MI from the 1986 tephra yield significantly different S, V, and Fe XANES spectra when compared to MI from the other eruptions, with disagreement between calculated  $fO_2$ 's from the three valence state oxybarometers beyond the uncertainty of the calibration models. Their V  $\mu$ -XANES spectra are also significantly more ordered and yield more reduced average V valence. The S  $\mu$ -XANES spectra display a significantly more intense low-energy spectral resonance, which indicates differences in Fe-S bonding character, and greater variability in their measured sulfate content. These V and S spectroscopic features are best explained by crystallization of sub-micrometer magnetite and sulfide crystallites within the 1986 inclusions. The sensitivity of XANES spectroscopy to short-range order allows these crystallites to be recognized even though they are not easily detected by imaging analysis. This shows that V and S  $\mu$ -XANES are potentially highly sensitive tools for identifying the presence of volumetrically minor amounts of spinel and sulfide within inclusions extracted from rapidly-cooled samples of tephra. Additionally, the observation that rehomogenized 1938 and 1948 inclusions from lava yield similar S, V, and Fe XANES spectra to the 2006 inclusions from tephra may be an encouraging indication that rehomogenization appears to have enabled the successful recovery of their pre-eruptive  $fO_2$ , despite their complex post-eruptive histories.

### **Biotic and Abiotic Retention, Recycling and Remineralization of Metals in the Ocean**

Publication: Philip W. Boyd, Michael J. Ellwood, Alessandro Tagliabue, Benjamin S. Twining (2017) **Nat. Geoscience** 10, 167-173. DOI: 10.1038/ngeo2876

Trace metals shape both the biogeochemical functioning and biological structure of oceanic provinces. Trace metal biogeochemistry has primarily focused on modes of external supply of metals from aeolian, hydrothermal, sedimentary and other sources. However, metals also undergo internal transformations such as abiotic and biotic retention, recycling and remineralization. The role of these internal transformations in metal biogeochemical cycling is now coming into focus. First, the retention of metals by biota in the surface ocean for days, weeks or months depends on taxon-specific metal requirements of phytoplankton, and on their ultimate fate: that is, viral lysis, senescence, grazing and/or export to depth. Rapid recycling of metals in the surface ocean can extend seasonal productivity by maintaining higher levels of metal bioavailability compared to the influence of external metal input alone. As metal-containing organic particles are exported from the surface ocean, different metals exhibit distinct patterns of remineralization with depth. These patterns are mediated by a wide range of physicochemical and microbial processes such as the ability of particles to sorb metals, and are influenced by the mineral and organic characteristics of sinking particles. We conclude that internal metal transformations play an essential role in controlling metal bioavailability, phytoplankton distributions and the subsurface resupply of metals.

### **Peridotites and Basalts Reveal Broad Congruence Between Two Independent Records of Mantle $fO_2$ Despite Local Redox Heterogeneity**

Publication: Suzanne K. Birner, Elizabeth Cottrell, Jessica M. Warren, Katherine A. Kelley, Fred A Davis (2018) **Earth Planet. Sci. Lett.** 494, 172-189. DOI: 10.1016/j.epsl.2018.04.035

The oxygen fugacity ( $fO_2$ ) of the oceanic upper mantle has fundamental implications for the production of magmas and evolution of the Earth's interior and exterior. Mid-ocean ridge basalts and peridotites sample the oceanic upper mantle, and retain a record of oxygen fugacity. While  $fO_2$  has been calculated for mid-ocean ridge basalts worldwide (>200 locations), ridge peridotites have been comparatively less well studied (33 samples from 11 locations), and never in the same geographic location as basalts. In order to determine whether peridotites and basalts from mid-ocean ridges record congruent information about the  $fO_2$  of the Earth's interior, we analyzed 31 basalts and 41 peridotites from the Oblique Segment of the Southwest Indian Ridge. By measuring basalts and peridotites from the same ridge segment, we can compare samples with maximally similar petrogenetic histories. We project the composition and oxygen fugacity of each lithology back to source conditions, and evaluate the effects of factors such as subsolidus diffusion in peridotites and fractional crystallization in basalts. We find that, on average, basalts and peridotites from the Oblique Segment both reflect a source mantle very near the quartz–fayalite–magnetite (QFM) buffer. However, peridotites record a significantly wider range of values (nearly 3 orders of magnitude in  $fO_2$ ), with a single dredge recording a range in  $fO_2$  greater than that previously reported for mid-ocean ridge peridotites worldwide. This suggests that mantle  $fO_2$  may be heterogeneous on relatively short length scales, and that this heterogeneity may be obscured within aggregated basalt melts. We further suggest that the global peridotite  $fO_2$  dataset may not provide a representative sample of average basalt-source mantle. Our study motivates further investigation of the  $fO_2$  recorded by ridge peridotites, as peridotites record information about the  $fO_2$  of the Earth's interior that cannot be gleaned from analysis of basalts alone.

### **Shock-Transformation of Whitlockite to Merrillite and the Implications for Meteoritic Phosphate**

Publication: C.T. Adcock, O. Tschauner, E.M. Hausrath, A. Udry, S.N. Luo, Y. Cai, M. Ren, A. Lanzirotti, M. Newville, M. Kunz, C. Lin (2017) **Nat. Commun.** 8, 14667-1-14667-8. DOI: 10.1038/ncomms14667

Meteorites represent the only samples available for study on Earth of a number of planetary bodies. The minerals within meteorites therefore hold the key to addressing numerous questions about our solar system. Of particular interest is the Ca-phosphate mineral merrillite, the anhydrous end-member of the merrillite–whitlockite solid solution series. For example, the anhydrous nature of merrillite in Martian meteorites has been interpreted as evidence of water-limited late-stage Martian melts. However, recent research on apatite in the same meteorites suggests higher water content in melts. One complication of using meteorites rather than direct samples is the shock compression all meteorites have experienced, which

can alter meteorite mineralogy. Here we show whitlockite transformation into merrillite by shock-compression levels relevant to meteorites, including Martian meteorites. The results open the possibility that at least part of meteoritic merrillite may have originally been H<sup>+</sup>-bearing whitlockite with implications for interpreting meteorites and the need for future sample return.

### Beamline 13-BM-C

#### **Isosymmetric Pressure-Induced Bonding Increase Changes Compression Behavior of Clinopyroxenes across Jadeite-Aegirine Solid Solution in Subduction Zones**

Publication: Jingui Xu, Dongzhou Zhang, Dawei Fan, Robert T. Downs, Yi Hu, Przemyslaw K. Dera (2017) *J. Geophys. Res.* 122 (1), 142-157. DOI: 10.1002/2016JB013502

Pyroxenes are among the most important minerals of Earth's crust and upper mantle and play significant role in controlling subduction at convergent margins. In this study, synchrotron-based single-crystal X-ray diffraction experiments were carried out on a natural aegirine [NaFe<sup>3+</sup>Si<sub>2</sub>O<sub>6</sub>] sample at ambient temperature and high pressures to 60 GPa, simulating conditions within the coldest part of a subduction zone consisting of old lithosphere. The diffraction data reveal no obvious sign of structural phase transition in aegirine within this pressure range; however, several relevant structural parameter trends change noticeably at approximately 24 GPa, indicating the presence of the previously predicted isosymmetric bonding change, related to increase of coordination number of Na<sup>+</sup> at M2 site. The pressure-volume data, fit with third-order Birch-Murnaghan (BM3) equation of state over the whole pressure range, yields  $K_{T0}=126(2)$  GPa and  $K'_{T0}=3.3(1)$ , while separate BM3 fits performed for the 0–24.0 GPa and 29.9–60.4 GPa pressure ranges give  $K_{T0}=118(3)$  GPa,  $K'_{T0}=4.2(3)$  and  $K_{T0}=133(2)$  GPa,  $K'_{T0}=3.0(1)$ , suggesting that the structure stiffens as a result of the new bond formation. Aegirine exhibits strong anisotropic compression with unit strain axial ratios  $\epsilon_1:\epsilon_2:\epsilon_3=1.00:2.44:1.64$ . Structural refinements reveal that NaO<sub>8</sub> polyhedron is the most compressible and SiO<sub>4</sub> tetrahedron has the lowest compressibility. The consequence of bonding transition is that the compressional behavior of aegirine below ~24 GPa and above that pressure is quite different, with likely consequences for relevant thermodynamic parameters and ion diffusion coefficients.

#### **FeO<sub>2</sub> and FeOOH under Deep Lower-Mantle Conditions and Earth's Oxygen–Hydrogen Cycles**

Publication: Qingyang Hu, Duck Young Kim, Wenge Yang, Liuxiang Yang, Yue Meng, Li Zhang, Hong-Kwang Mao (2016), *Nature* 534, 241-244. DOI: 10.1038/nature18018

The distribution, accumulation and circulation of oxygen and hydrogen in Earth's interior dictate the geochemical evolution of the hydrosphere, atmosphere and biosphere. The oxygen-rich atmosphere and iron-rich core represent two end-members of the oxygen–iron (O–Fe) system, overlapping with the entire pressure–temperature–composition range of the planet. The extreme pressure and temperature conditions of the deep interior alter the oxidation states, spin states and phase stabilities of iron oxides, creating new stoichiometries, such as Fe<sub>4</sub>O<sub>5</sub> and Fe<sub>5</sub>O<sub>6</sub>. Such interactions between O and Fe dictate Earth's formation, the separation of the core and mantle, and the evolution of the atmosphere. Iron, in its multiple oxidation states, controls the oxygen fugacity and oxygen budget, with hydrogen having a key role in the reaction of Fe and O (causing iron to rust in humid air). We used first-principles calculations and experiments to identify a highly stable, pyrite-structured iron oxide (FeO<sub>2</sub>) at 76 gigapascals and 1,800 kelvin that holds an excessive amount of oxygen. We show that the mineral goethite, FeOOH, which exists ubiquitously as 'rust' and is concentrated in bog iron ore, decomposes under the deep lower-mantle conditions to form FeO<sub>2</sub> and release H<sub>2</sub>. The reaction could cause accumulation of the heavy FeO<sub>2</sub>-bearing patches in the deep lower mantle, upward migration of hydrogen, and separation of the oxygen and hydrogen cycles. This process provides an alternative interpretation for the origin of seismic and geochemical anomalies in the deep lower mantle, as well as a sporadic O<sub>2</sub> source for the Great Oxidation Event over two billion years ago that created the present oxygen-rich atmosphere.

#### **Thermal Equation of State of Natural Ti-Bearing Clinohumite**

Publication: Fei Qin, Xiang Wu, Dongzhou Zhang, Shan Qin, Steven D. Jacobsen (2017) *J. Geophys. Res.* 122 (11), 8943-8951. DOI: 10.1002/2017JB014827

The natural occurrence of clinohumite in metabasalts and hydrothermally altered peridotites provides a source of water-rich minerals in subducted slabs, making knowledge of their phase relations and crystal chemistry under high pressure-temperature (P-T) conditions important for understating volatile recycling and geodynamic process in the Earth's mantle. We conducted a synchrotron-based, single-crystal X-ray

diffraction study on two natural Ti-bearing clinohumites up to ~28 GPa and 750 K in order to simulate conditions within subducted slabs. No phase transition occurs in clinohumite over this P-T range. Pressure-volume relationships of both compositions at room temperature were fitted to a third-order Birch-Murnaghan equation of state (EoS) with  $V_0 = 650.4(3) \text{ \AA}^3$ ,  $K_{T0} = 141(4) \text{ GPa}$ , and  $K_{T0}' = 4.0(6)$  for Ti-poor clinohumite (0.07 Ti per formula unit, pfu) and  $V_0 = 650.8(3) \text{ \AA}^3$ ,  $K_{T0} = 144(4) \text{ GPa}$ , and  $K_{T0}' = 3.6(7)$  for Ti-rich clinohumite (0.21 Ti pfu). Both clinohumites exhibit anisotropic compression with  $\beta_b > \beta_c > \beta_a$ . We also refined P-V-T equation of state parameters using the high-temperature Birch-Murnaghan EoS, yielding  $(\partial K_{T0}/\partial T)_P = -0.040(10) \text{ GPa/K}$  and  $\alpha_T = 5.1(6) \times 10^{-5} \text{ K}^{-1}$  for Ti-poor clinohumite and  $(\partial K_{T0}/\partial T)_P = -0.045(11) \text{ GPa/K}$  and  $\alpha_T = 5.7(6) \times 10^{-5} \text{ K}^{-1}$  for Ti-rich clinohumite. Ti-poor and Ti-rich clinohumites display similar equations of state but are ~20% more incompressible than Mg-pure clinohumite and display ~5% higher bulk sound velocity than olivine at upper mantle conditions. Our results provide constraints for modeling geodynamic process related to the subduction and transport of potentially water-rich slabs in the mantle.

### **Changes in the Structure of Birnessite during Siderophore-Promoted Dissolution: A Time-Resolved Synchrotron X-ray Diffraction Study**

Publication: Timothy B. Fischer, Peter J. Heaney, Jeffrey E. Post (2018). *Chem. Geol.* 476, 46-58, DOI: 10.1016/j.chemgeo.2017.11.003

We used time-resolved synchrotron X-ray diffraction to follow the complete dissolution of synthetic triclinic Na-birnessite as promoted by the trihydroxamate siderophore desferrioxamine B (DFOB). Many microorganisms employ siderophores to increase the availability of Fe, Mn, and other trace metals for metabolic processes. Our primary goal was to quantify the DFOB-assisted dissolution rate by direct, continuous observation of the solid phase. Our kinetic model indicates that the rate of dissolution is dependent on [DFOB] but not pH, and has a reaction order of 0.505 with a rate constant of 0.112 wt% birn  $\text{min}^{-1}$ . The unit-cell dimensions of birnessite remained virtually constant within error throughout the dissolution process, showing only a 0.3% contraction along the c-axis.

Despite the small changes in unit-cell volume, Rietveld analysis revealed that the occupancy of Mn within the octahedral sheets decreased from 100% to ~80%, presumably as the result of complexation of structural  $\text{Mn}^{3+}$  with DFOB followed by extraction of  $\text{Mn}^{3+}$  from the crystal structure. These observations suggest a critical lacunarity of ~20 mol% Mn for triclinic Na-birnessite, below which the structure is destabilized. Moreover, this study reveals that DFOB-promoted dissolution must operate by a different mechanism from that engaged when bacterial membrane fractions directly transfer electrons to birnessite crystals. We propose that crystal structure analysis of minerals undergoing dissimilatory metal reduction can elucidate metabolic pathways employed by microorganisms.

### **Mineral–Water Interface Structure of Xenotime (YPO<sub>4</sub>) {100}**

Publication: Andrew G. Stack, Joanne E. Stubbs, Sriram G. Srinivasan, Santanu Roy, Vyacheslav S. Bryantsev, Peter J. Eng, Radu Custelcean, Alexander D. Gordon, Cole R. Hexel (2018) *J. Phys. Chem. C* 122 (35), 20232-20243. DOI: 10.1021/acs.jpcc.8b04015

Crystal truncation rod (CTR) measurements and density functional theory (DFT) calculations were performed to determine the atomic structure of the mineral–water interface of the {100} surface of xenotime (nominally YPO<sub>4</sub>). This mineral is important, because it incorporates a variety of rare earth elements (REEs) in its crystal structure. REEs are critical materials necessary for a variety of renewable and energy efficient technologies. Current beneficiation techniques are not highly selective for REE ore minerals, and large amounts go to waste; this is a first step toward designing more efficient beneficiation. Evidence is found for minor relaxation of the surface within the topmost monolayer with little or no relaxation in subsurface layers. Justification for ordered water at the interface is found, where water binds to surface cations and donates hydrogen bonds to surface phosphates. The average bond lengths between cations and oxygens on water are 228 pm in the best fit to the CTR data, versus 243 and 251 pm for the DFT. No agreement on water positions bound to surface phosphates is obtained. Overall, the findings suggest that ligands used in

beneficiation with a single anionic headgroup, such as fatty acids, will have limited selectivity for xenotime relative to undesirable minerals.

### **Valence and Spin States of Iron are Invisible in Earth's Lower Mantle**

Publication: Liu, J., Dorfman, S.M., Zhu, F., Li, J., Wang, Y., Zhang, D., Xiao, Y., Bi, W., and Alp, E.E. (2018), **Nature Communications**, 9, 1284. DOI: 10.1038/s41467-018-03671-5

Heterogeneity in Earth's mantle is a record of chemical and dynamic processes over Earth's history. The geophysical signatures of heterogeneity can only be interpreted with quantitative constraints on effects of major elements such as iron on physical properties including density, compressibility, and electrical conductivity. However, deconvolution of the effects of multiple valence and spin states of iron in bridgmanite (Bdg), the most abundant mineral in the lower mantle, has been challenging. Here we show through a study of a ferric-iron-only ( $\text{Mg}_{0.46}\text{Fe}^{3+}_{0.53}$ )( $\text{Si}_{0.49}\text{Fe}^{3+}_{0.51}$ ) $\text{O}_3$  Bdg that  $\text{Fe}^{3+}$  in the octahedral site undergoes a spin transition between 43 and 53 GPa at 300 K. The resolved effects of the spin transition on density, bulk sound velocity, and electrical conductivity are smaller than previous estimations, consistent with the smooth depth profiles from geophysical observations. For likely mantle compositions, the valence state of iron has minor effects on density and sound velocities relative to major cation composition.

### **High-Pressure Gamma-CaMgSi<sub>2</sub>O<sub>6</sub>: Does Penta-Coordinated Silicon Exist in the Earth's Mantle?**

Publication: Hu, Y., Kiefer, B., Bina, C.R., Zhang, D. and Dera, P.K. (2017), **Geophysical Research Letters**, 44, 11340-11348. DOI: 10.1002/2017GL075424

In situ X-ray diffraction experiments with natural Fe- and Al- bearing diopside single crystals and density functional theory (DFT) calculations on diopside end-member composition indicate the existence of a new high-pressure  $\gamma$ -diopside polymorph with rare penta-coordinated silicon. On compression  $\alpha$ -diopside transforms to the  $\gamma$ -phase at  $\sim 50$  GPa, which in turn, on decompression is observed to convert to the known  $\beta$ -phase below 47 GPa. The new  $\gamma$ -diopside polymorph constitutes another recent example of penta-coordinated silicon ( $^{\text{V}}\text{Si}$ ) in overcompressed metastable crystalline silicates, suggesting that  $^{\text{V}}\text{Si}$  may exist in the transition zone and the uppermost lower mantle in appreciable quantities, not only in silicate glass and melts but also in crystalline phases contained in the coldest parts of subducted stagnant slabs.  $^{\text{V}}\text{Si}$  may have significant influences on buoyancy, wave velocity anomalies, deformation mechanisms, chemical reactivity of silicate rocks, and seismicity within the slab.

### **Dehydrogenation of Goethite in Earth's Deep Lower Mantle**

Publication: Hu, Q., Kim, D.Y., Liu, J., Meng, Y., Yang, L., Zhang, D., Mao, W.L., and Mao, H.-K. (2017), **PNAS**, 114(7), 1498-1501. DOI: 10.1073/pnas.1620644114

The cycling of hydrogen influences the structure, composition, and stratification of Earth's interior. Our recent discovery of pyrite-structured iron peroxide (designated as the P phase) and the formation of the P phase from dehydrogenation of goethite  $\text{FeO}_2\text{H}$  implies the separation of the oxygen and hydrogen cycles in the deep lower mantle beneath 1,800 km. Here we further characterize the residual hydrogen,  $x$ , in the P-phase  $\text{FeO}_2\text{H}_x$ . Using a combination of theoretical simulations and high-pressure-temperature experiments, we calibrated the  $x$  dependence of molar volume of the P phase. Within the current range of experimental conditions, we observed a compositional range of P phase of  $0.39 < x < 0.81$ , corresponding to 19–61% dehydrogenation. Increasing temperature and heating time will help release hydrogen and lower  $x$ , suggesting that dehydrogenation could be approaching completion at the high-temperature conditions of the lower mantle over extended geological time. Our observations indicate a fundamental change in the mode of hydrogen release from dehydration in the upper mantle to dehydrogenation in the deep lower mantle, thus differentiating the deep hydrogen and hydrous cycles.

## Beamline 13-BM-D

### **Dehydration-Driven Stress Transfer Triggers Intermediate-Depth Earthquakes**

Publication: Thomas P. Ferrand, Nadege Hilairet, Sarah Incel, Damien Deldicque, Loic Labrousse, Julien Gasc, Joerg Renner, Yanbin Wang, Harry W. Green II, Alexandre Schubnel (2017), **Nat. Commun.** 8, 15247-1-15247-11. DOI: 10.1038/ncomms15247

Intermediate-depth earthquakes (30–300 km) have been extensively documented within subducting oceanic slabs, but their mechanics remains enigmatic. Here we decipher the mechanism of these earthquakes by performing deformation experiments on dehydrating serpentized peridotites (synthetic antigorite-olivine aggregates, minerals representative of subduction zones lithologies) at upper mantle conditions. At a pressure of 1.1 gigapascals, dehydration of deforming samples containing only 5 vol% of antigorite suffices to trigger acoustic emissions, a laboratory-scale analogue of earthquakes. At 3.5 gigapascals, acoustic emissions are recorded from samples with up to 50 vol% of antigorite. Experimentally produced faults, observed post-mortem, are sealed by fluid-bearing micro-pseudotachylytes. Microstructural observations demonstrate that antigorite dehydration triggered dynamic shear failure of the olivine load-bearing network. These laboratory analogues of intermediate-depth earthquakes demonstrate that little dehydration is required to trigger embrittlement. We propose an alternative model to dehydration-embrittlement in which dehydration-driven stress transfer, rather than fluid overpressure, causes embrittlement.

### **Anomalous Density and Elastic Properties of Basalt at High Pressure: Reevaluating of the Effect of Melt Fraction on Seismic Velocity in the Earth's Crust and Upper Mantle**

Publication: Alisha N. Clark, Charles E. Lesher, Steven D. Jacobsen, Yanbin Wang (2016), **J. Geophys. Res.** 121 (8), 4232-4248. DOI: 10.1002/2016JB012973

Independent measurements of the volumetric and elastic properties of Columbia River basalt glass were made up to 5.5 GPa by high-pressure X-ray microtomography and GHz-ultrasonic interferometry, respectively. The Columbia River basalt displays P and S wave velocity minima at 4.5 and 5 GPa, respectively, violating Birch's law. These data constrain the pressure dependence of the density and elastic moduli at high pressure, which cannot be modeled through usual equations of state nor determined by stepwise integrating the bulk sound velocity as is common practice. We propose a systematic variation in compression behavior of silicate glasses that is dependent on the degree of polymerization and arises from the flexibility of the aluminosilicate network. This behavior likely persists into the liquid state for basaltic melts resulting in weak pressure dependence for P wave velocities perhaps to depths of the transition zone. Modeling the effect of partial melt on P wave velocity reductions suggests that melt fraction determined by seismic velocity variations may be significantly overestimated in the crust and upper mantle.

### **Application of Seismological Methodology to Acoustic Emission Experiments in Understanding Mechanisms of Faulting During the Olivine-Spinel Phase Transition**

Publication: Yanbin Wang, Lupei Zhu, Feng Shi, Alexandre Schubnel, Nadege Hilairet, Tony Yu, Mark L. Rivers, Julien Gasc, Fabrice Brunet (2017) **Sci. Adv.**, 3, e1601896, DOI: 10.1126/sciadv.1601896.

In collaboration with seismologist Lupei Zhu (St. Louis Univ.), we applied hypoDD algorithm for earthquake locations to acoustic emission (AE) data, increasing spatial resolution of AE events by a factor of 10 or more. Waveform correlation analyses also increased AE detection power by one order of magnitude. Development of microruptures during deformation/transformation are tracked in 4D in our experiments, allowing nucleation and growth mechanisms of fault propagation to be studied in unprecedented details. State-of-the-art seismological methodologies are also applied to AE records (nanoseismograms) to extract focal mechanisms, slip direction, and magnitudes. This collaboration resulted a funded CSEDI proposal for nanoseismology in the laboratory, involving post-docs at GSECARS and students at SLU..

### **Elasticity of Single-Crystal Superhydrous Phase B at Simultaneous High Pressure-Temperature Conditions**

Publication: Xinyang Li, Zhu Mao, Ningyu Sun, Yifan Liao, Shuangmeng Zhai, Yi Wang, Huaiwei Ni, Jingyun Wang, Sergey N. Tkachev, Jung-Fu Lin (2016) **Geophys. Res. Lett.** 43 (16), 8458-8465. DOI: 10.1002/2016GL070027

We investigated the combined effect of pressure and temperature on the elasticity of single-crystal superhydrous phase B (Shy-B) using Brillouin scattering and X-ray diffraction up to 12 GPa and 700 K. Using the obtained elasticity, we modeled the anisotropy of Shy-B along slab geotherms, showing that Shy-B has a low anisotropy and cannot be the major cause of the observed anisotropy in the region. Modeled velocities of Shy-B show that Shy-B will be shown as positive velocity anomalies at the bottom transition zone. Once Shy-B is transported to the topmost lower mantle, it will exhibit a seismic signature of lower velocities than topmost lower mantle. We speculate that an accumulation of hydrous phases, such as Shy-B, at the topmost lower mantle with a weight percentage of ~17–26% in the peridotite layer as subduction progresses could help explain the observed 2–3% low shear velocity anomalies in the region.

### **Hotspots of Soil N<sub>2</sub>O Emission Enhanced through Water Absorption by Plant Residue**

Publication: A.N. Kravchenko, E.R. Toosi, A.K. Guber, N.E. Ostrum, J. Yu, K. Azeem, M.L. Rivers, G.P. Robertson (2017) **Nat. Geoscience** 10, 496-500. DOI: 10.1038/ngeo2963

N<sub>2</sub>O is a highly potent greenhouse gas and arable soils represent its major anthropogenic source. Field-scale assessments and predictions of soil N<sub>2</sub>O emission remain uncertain and imprecise due to the episodic and microscale nature of microbial N<sub>2</sub>O production, most of which occurs within very small discrete soil volumes. Such hotspots of N<sub>2</sub>O production are often associated with decomposing plant residue. Here we quantify physical and hydrological soil characteristics that lead to strikingly accelerated N<sub>2</sub>O emissions in plant residue-induced hotspots. Results reveal a mechanism for microscale N<sub>2</sub>O emissions: water absorption by plant residue that creates unique micro-environmental conditions, markedly different from those of the bulk soil. Moisture levels within plant residue exceeded those of bulk soil by 4–10-fold and led to accelerated N<sub>2</sub>O production via microbial denitrification. The presence of large ( $\varnothing > 35 \mu\text{m}$ ) pores was a prerequisite for maximized hotspot N<sub>2</sub>O production and for subsequent diffusion to the atmosphere. Understanding and modelling hotspot microscale physical and hydrologic characteristics is a promising route to predict N<sub>2</sub>O emissions and thus to develop effective mitigation strategies and estimate global fluxes in a changing environment.

### **An Early Chondrichthyan and the Evolutionary Assembly of a Shark Body Plan**

Publication: Michael I. Coates, John A. Finarelli, Ivan J. Sansom, Plamen S. Andreev, Katharine E. Criswell, Kristen Tietjen, Mark L. Rivers, Patrick J. La Riviere (2018) **Proc. Roy. Soc. B. -- Biol. Sci.** 285 (1870), 1-10. DOI: 10.1098/rspb.2017.2418

Although relationships among the major groups of living gnathostomes are well established, the relatedness of early jawed vertebrates to modern clades is intensely debated. Here, we provide a new description of Gladbachus, a Middle Devonian (Givetian approx. 385-million-year-old) stem chondrichthyan from Germany, and one of the very few early chondrichthyans in which substantial portions of the endoskeleton are preserved. Tomographic and histological techniques reveal new details of the gill skeleton, hyoid arch and jaws, neurocranium, cartilage, scales and teeth. Despite many features resembling placoderm or osteichthyan conditions, phylogenetic analysis confirms Gladbachus as a stem chondrichthyan and corroborates hypotheses that all acanthodians are stem chondrichthyans. The unfamiliar character combination displayed by Gladbachus, alongside conditions observed in acanthodians, implies that pre-Devonian stem chondrichthyans are severely under-sampled and strongly supports indications from isolated scales that the gnathostome crown group originated at the latest by the early Silurian (approx. 440 Ma). Moreover, phylogenetic results highlight the likely convergent evolution of conventional chondrichthyan conditions among earliest members of this primary gnathostome division, while skeletal morphology points towards the likely suspension feeding habits of Gladbachus, suggesting

a functional origin of the gill slit condition characteristic of the vast majority of living and fossil chondrichthyans.

### **2.3. Partner Users and CAT Members**

GSECARS has no Partner Users or CAT Members that receive guaranteed beam time. As described previously, COMPRES is contributing to the DAC program on station 13-BM-C, but does not receive any guaranteed beam time in return.

### **2.4. General User Program**

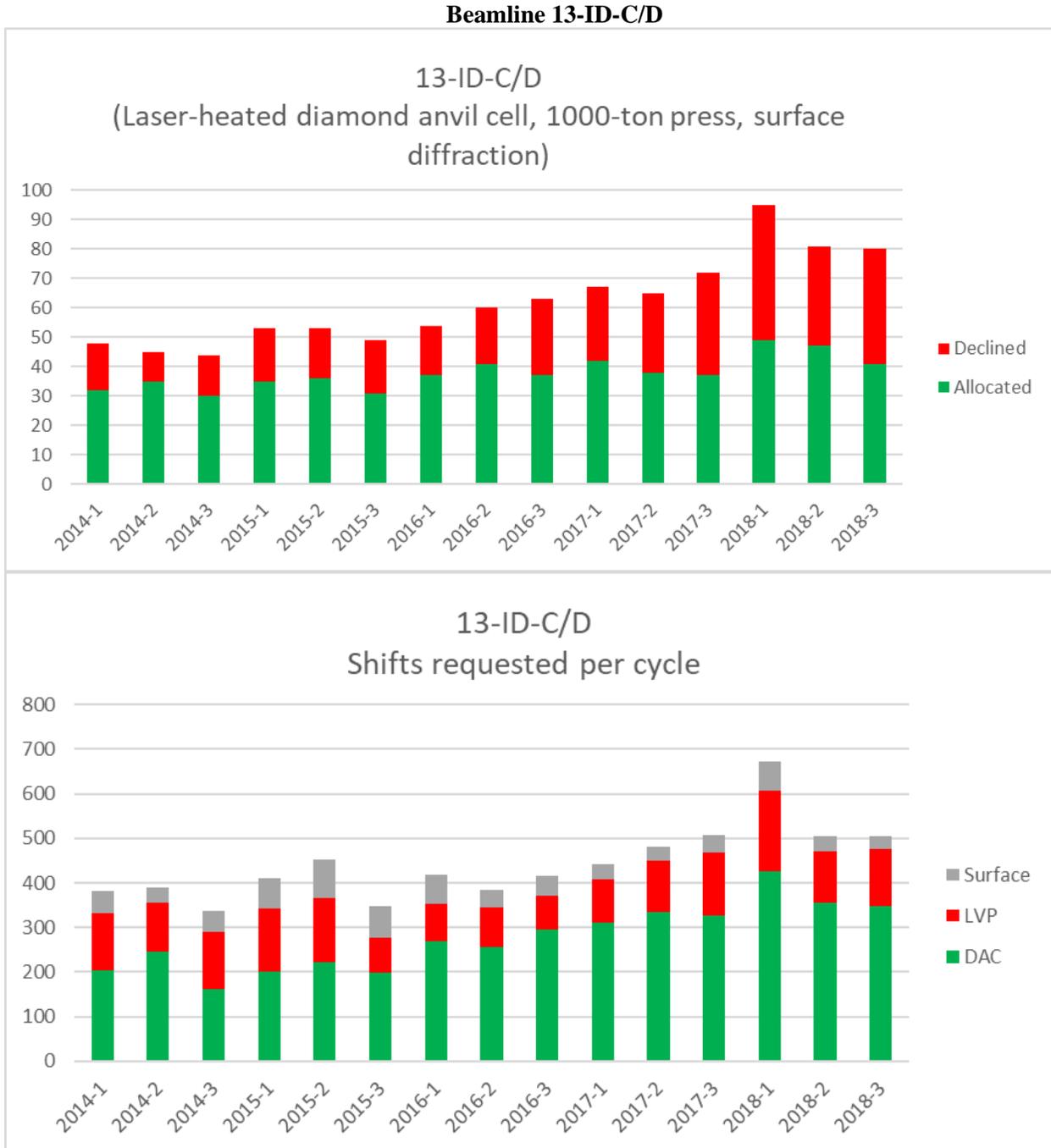
The GSECARS User Program has been in full operation since Fall 1998. Essentially 100% of the available user operations beam time is being allocated through the APS General User Program. The APS Beamtime Allocation Committee (BAC) allocates 25% of the available time, and GSECARS allocates the remaining 75% based largely on ratings from the APS Proposal Review Panels (PRPs). Research at GSECARS has resulted in over 1,866 publications in the APS database including PhD and Masters theses.

The GSECARS sector is oversubscribed on all stations, with the oversubscription for 2018 ranging from 1.1 (13BM-D) to 2.9 (13ID-C/D). The oversubscription factor is defined to be the ratio of the number of days requested by users (Sector 13 first choice) to the number of days available to users. We handle this oversubscription by limiting the number of days each experiment receives, rejecting experiments, and referring experiments to other suitable synchrotron facilities. The challenge has been to balance the desire to give beam time to as many highly rated proposals as possible while providing sufficient beam time to each experiment to accomplish the intended goals. The proposal success rate is ~60%. The beamtime demand is discussed further in the following section.

GSECARS users come from all over the world: 76% are from the USA, 11% from Europe, 7% from Canada, and 6% from Asia and Australia. 83% of the investigators are affiliated with universities; 6% with government laboratories (e.g., national laboratories); 1% with other government agencies (e.g., USGS, EPA); 9% with private institutions (e.g., Carnegie Institution of Washington); and 1% with industry. GSECARS staff work with prospective users to help them submit beam time proposals, to prepare samples before they arrive, to collect their data, and to analyze the data and prepare it for publication after they leave the facility. Most publications resulting from work at GSECARS include one or more GSECARS beamline scientists as co-authors. About 62% of the GSECARS users are students or postdocs at universities and colleges. Thus, the level of student and postdoc participation at GSECARS is very high.

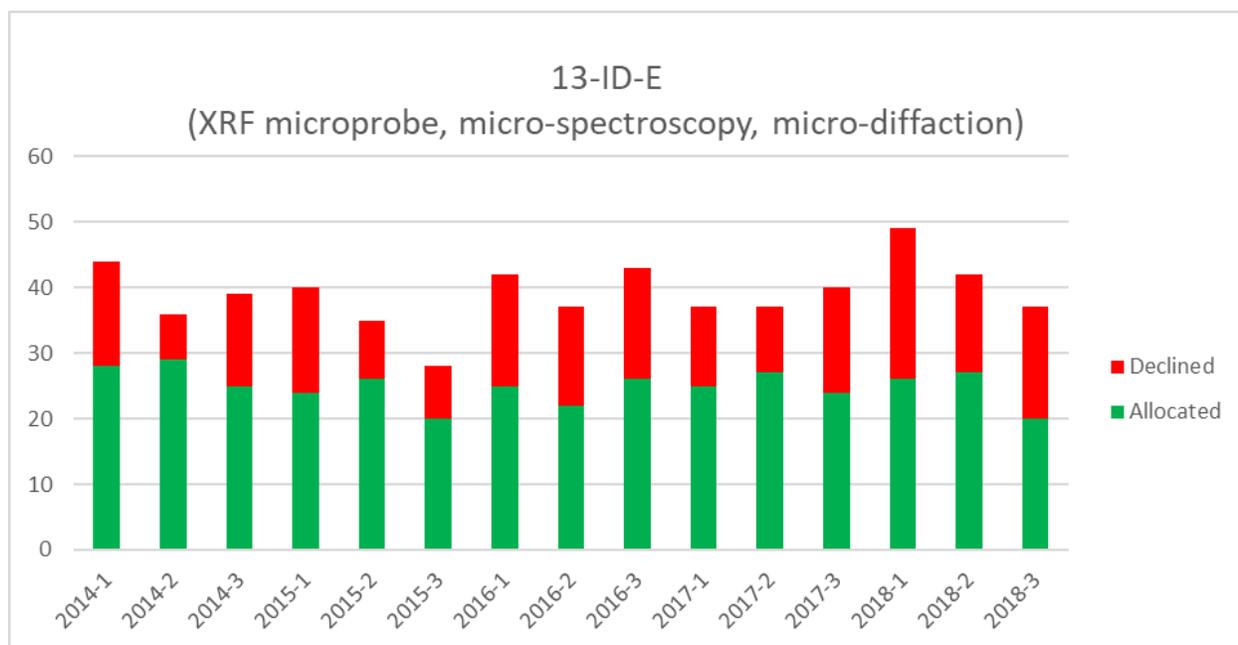
## 2.5. Trends in Beamtime Demand

The following figures show the variation in beam time requests for the past 5 years. The first plot for each beamline shows the number of beamtime requests that were allocated time, and the number that were declined. The second plot shows the number of shifts requested for each technique. There are approximately 200 shifts available for user time in each cycle (3 cycles per year).



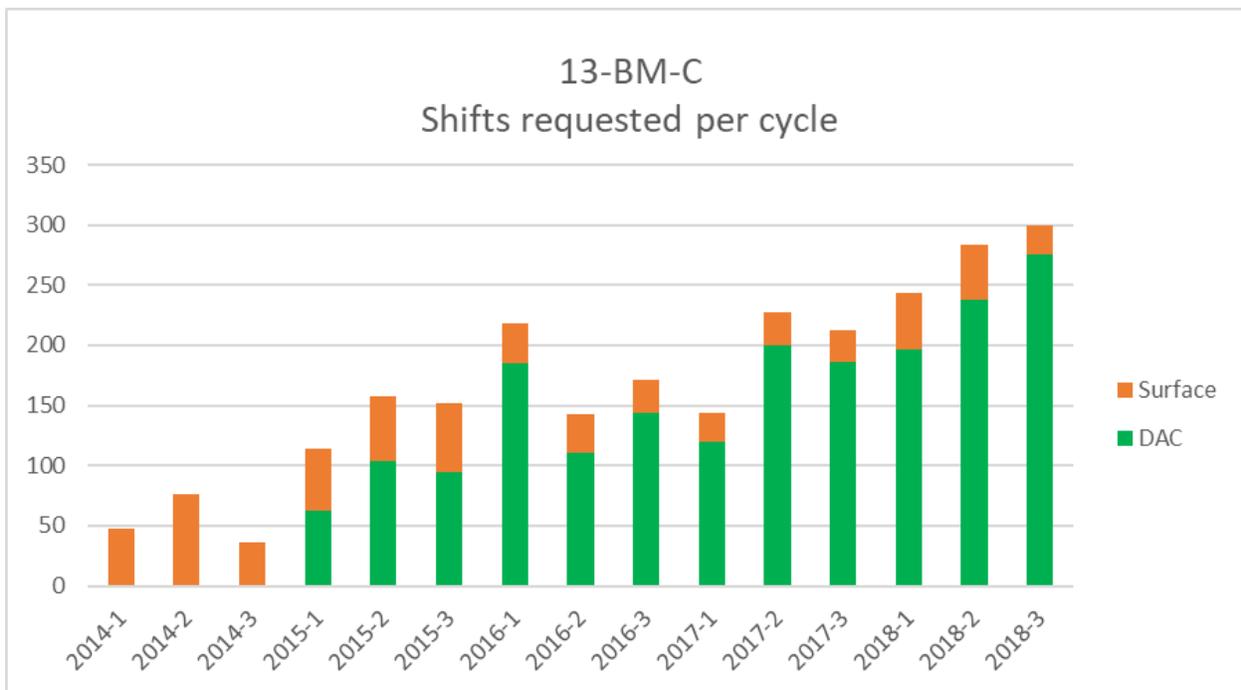
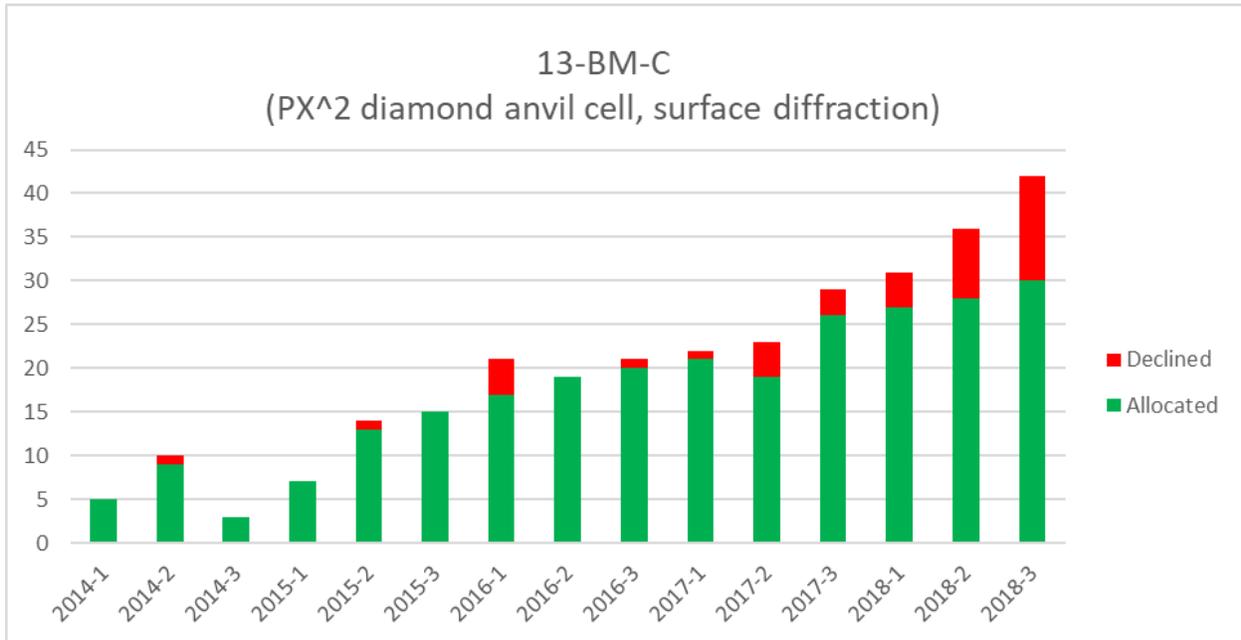
On 13ID-C/D the allocated proposals have increased from ~32 to ~45 per cycle, while the declined proposals have increased from ~15 to ~40 per cycle. Requested shifts have increased from ~350 to ~500. Most of this increase is in the DAC program, and most DAC proposals now only receive 3 shifts (1 day)

### Beamline 13-ID-E



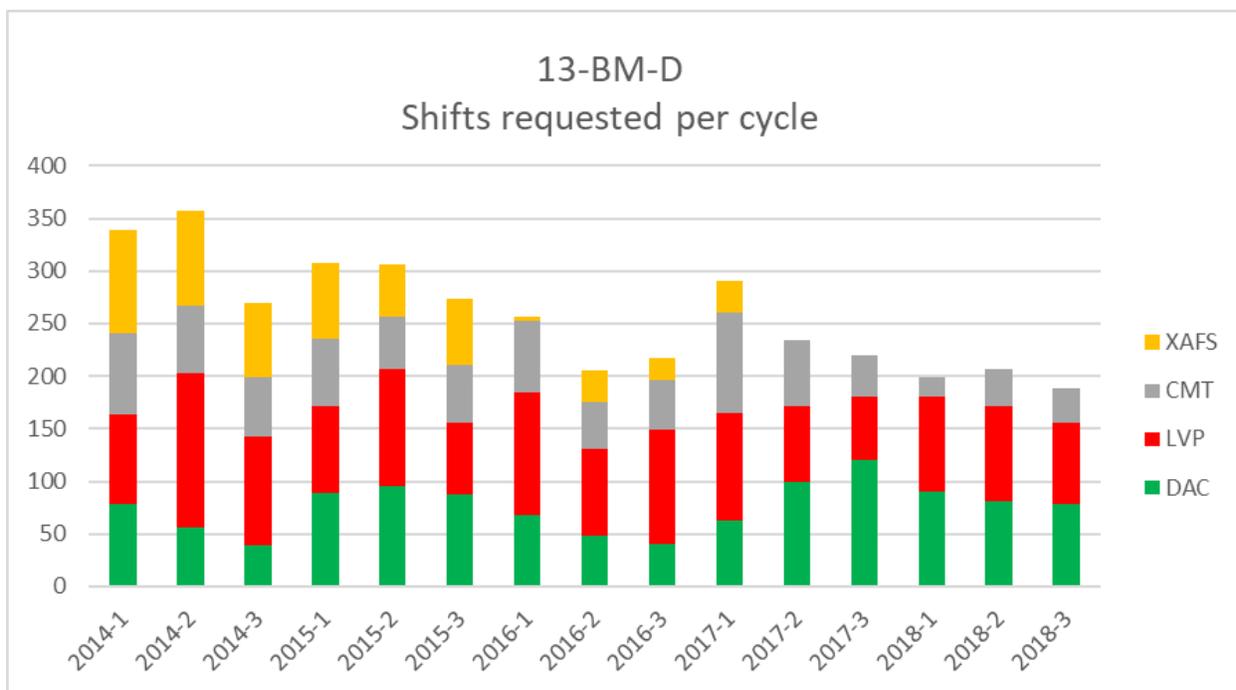
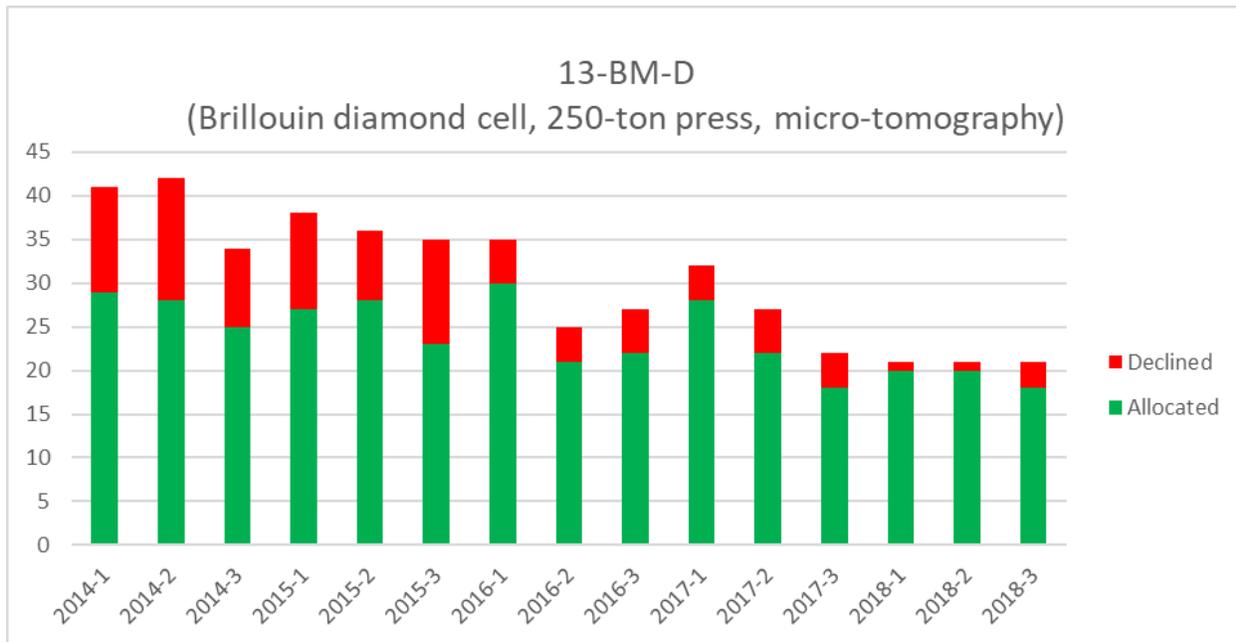
Demand for 13ID-E has been rather steady over this 5-year period. The techniques on this station (micro-XRF/XAS/diffraction) are often all used for each experiment so we have not produced a plot by technique.

### Beamline 13-BM-C



The PX2 partnership on 13BM-C began in 2015-2. Since then the DAC proposals have been steadily increasing, and the oversubscription is now ~1.5.

### Beamline 13-BM-D



Demand for bulk XAFS on 13-BM-D declined significantly from 2014-2017. Beginning in 2017-2 we decided to no longer offer this technique. Demand for tomography has also decreased somewhat. This station is the only one for which oversubscription is decreasing. We are planning to enhance the tomography program to focus on time-resolved studies, and are looking to grow the LVP community, potentially with another collaboration with COMPRES.

## 2.6. Enhancements since 2014 SAC Review

The following is a brief description of the enhancements since the 2014 SAC Review.

**13-ID-C/D:** In early 2018, we purchased a Pilatus3 X 300K-W CdTe detector with a rectangular format, 1475x195 pixels. This detector is largely for use in amorphous scattering experiments with the DAC and Paris-Edinburgh cell and the Soller slit assembly, for which this is an ideal form factor.

**13-ID-D:** In collaboration with ChemMatCARS (sector 15) in 2016 we purchased a Pilatus3 X 1M CdTe detector. GSECARS has 40% use of this detector, mainly for diffraction experiments with the laser-heated DAC in 13-ID-D. This detector replaced a marCCD. It has a much faster readout, up to 500 frames/s, and no readout noise.

**13-ID-E:** In 2014 we upgraded our fluorescence detection system to include new pulse-processing electronics from Quantum Detectors. This new Xspress 3 digital X-ray processor system provided dramatic enhancements for fluorescence-based mapping and spectroscopy, maximizing output count rate through automated adaptive filtering, rather than the more conventional use of fixed shaping or peaking times used in the previous XMap based electronics. This optimizes the output for each sample for mapping and spectroscopy applications without user intervention. These electronics also allowed us to implement continuous energy scanning in fluorescence mode, which improves data collection efficiency and data quality compared to step scanning. This mode requires coordinated motion of monochromator angle and gap between 1<sup>st</sup> and 2<sup>nd</sup> crystals to maintain fixed beam height, which can be synchronized in hardware. It also requires synchronization of the monochromator energy and the undulator energy, which cannot currently be synchronized at the hardware level, and must be done in software. This software synchronization and mechanical limitations of the undulator currently limits the per-energy time for energy scans to about 0.5 seconds. Despite this limitation, continuous energy scanning is now the standard method for collecting XANES and EXAFS and is transparent to the users.

We recently purchased and received a Dectris Eiger 500K detector for use with fast diffraction mapping. This detector can do over 5,000 frames/s and will replace a Perkin Elmer 1621 that was limited to 15 frames/s in full resolution, or 30 frames/s with 2x2 binning. We have also installed an offline optical microscope system with encoded sample stage for recording sample analysis locations prior to beam time sessions. This system is located in the 13-ID-E control area for easy access by users.

**13-BM-C:** We have added a 200 mm long horizontal focusing mirror to 13-BM-C for microfocusing in the diamond anvil cell. With PX2 we have also added an online optical microscope, Raman/ruby fluorescence system, remote membrane pressure controller, and 200 watt laser heating system. The PX2 experiments are done on the same large 6-circle Newport diffractometer that is used for the surface science measurements in this station.

In 2017 PX2 funded a 3-axis translational stage system with Newport ESP motor controllers and a FLIR Point Grey camera, which serves as a radiography imaging system. The radiography setup provides accurate sample alignment capability to carry out single crystal diffraction on natural host-inclusion samples with irregular shape.

To date the DAC single-crystal measurements have used a mar165 CCD detector. This has the disadvantage that it requires a shutter when reading out the detector, and has a 3 second readout time. GSECARS and COMPRES have recently purchased a Pilatus 1M detector with a 1 mm silicon sensor. The detector can run at 25 frames/s, and does not require a shutter. This detector has arrived and will be commissioned during the 2018-3 run cycle.

**13-BM-D:** We replaced our Roper CoolSnap detector with a fast CMOS camera from Point Grey. This has lower readout noise, higher dynamic range, and a much higher frame rate, up to 163 frames/s. This has allowed us to begin to offer pink-beam tomography where we can collect an entire 900 projection

dataset in under 10 seconds. This is being used to do time-resolved imaging for fluid flow, mechanical loading, etc. This beamline has a 1m long vertical mirror with white-beam capability, so we can remove higher energy x-rays. The mirror can also be bent to defocus the beam, providing a large vertical field of view, even at very high energy.

**Lab-Office Module:** We are now using part of the Sector 14 laboratory space which has been outfitted as a dedicated DAC sample preparation laboratory. A micromanipulator system was installed in the Sector 13 laser lab to support the manipulation of minute experimental components and samples. The hallway between Sectors 13 and 14 was outfitted with additional user desk space.

A new advanced integrated optical system was built in collaboration with the Carnegie Institution of Washington and is currently in the final stage of commissioning. It will be available for users by the end of this year. In this system we have implemented Raman spectroscopy with five excitation wavelengths (266, 473, 532, 660, 946 nm), confocal imaging, double sided IR laser heating combined with high temperature Raman (including coherent anti-Stokes Raman scattering) and transient (based on a bright supercontinuum light source) spectroscopies in a wide spectral range (200-1600 nm).

## 2.7. Outreach/Expansion Initiatives

GeoSoilEnviroCARS operates as a national research resource for the entire earth, planetary, soil and environmental science communities. GSECARS uses a team approach, where lead individuals (scientists, engineers and technicians) from GSECARS work together with instrument companies and machine shops to design and build the complex array of components that go into a synchrotron beamline. During this process, we are able to welcome students at all levels— high school, undergraduate, graduate and post graduate— into our laboratory giving them the opportunity to learn about X-ray science and instrumentation as well as to be involved in hands-on activities in which they can experiment at building and testing instruments.

The proposal-based beam time allocation system facilitates the use of this technology by experts and novices alike. Training provided by the experienced GSECARS staff results in direct knowledge transfer to advance the quality of the nation's research infrastructure and to enhance the educational experience of students. Students trained under this program come from educational institutions across the nation and around the world, including the participation of underrepresented groups. GSECARS and its staff have a history of conducting workshops to instruct qualified individuals in the theoretical and practical aspects of synchrotron radiation techniques in use at the APS. We also host programs to introduce underrepresented minorities, women, and young students to synchrotron research. Recent examples of such activities by GSECARS include:

- Organized (with Miami University) XAFS Mini Workshop (2015)
- Organized a workshop at GSECARS (with ENS Paris) on applications of acoustic emission in synchrotron-based deformation experiments (2016)
- Co-organized a mini workshop at St. Louis Univ. on applications of seismological methods in acoustic experiments (2018)
- Participation in the NSF REU Program. The Research Experiences for Undergraduates (REU) program supports active research participation by undergraduate students in any of the areas of research funded by the National Science Foundation. REU projects involve students in meaningful ways in ongoing research programs or in research projects specifically designed for the REU program. (2015, 2017)
- Participation in the DOE INCREASE Workshop (Interdisciplinary Consortium for Research and Educational Access in Science and Engineering). INCREASE is a consortium of universities whose mission is to promote research and education in Minority-Serving Institutions, especially as regards increasing their utilization of national user facilities, thereby increasing the numbers of women and those from historically underrepresented groups who pursue science and engineering careers. (2015)

- Participation each year in the APS/IIT XAFS School (Matt Newville, guest instructor)
- Participation each year in the ANL Science Careers in Search of Women event.
- Participation each year in the ANL Introduce a Girl to Engineering Day event.
- Hosted a workshop on Acoustic Emission, which is a technique available at GSECARS in the multi-anvil presses (2016)
- Hosted Exemplary Student Research Program (ESRP) where local high school students conduct hands-on research and present posters at the APS User Meeting (2016., 2018)
- Participation in the APS/SNS X-ray/Neutron School with hands-on labs (2015, 2016)
- Helped sponsor the 2018 Workshop of the IUCr Commission on High Pressure. The purpose of the 2018 workshop was to bring together researchers who apply tools of extreme-conditions crystallography to different disciplines of science.
- Co-hosted a hands-on workshop dedicated to demonstrating the techniques and future developments of micro-manipulator using the Axis Pro Micromanipulation System. (2018)

### 3. Current Staff

	<b>Position</b>
<b>Scientific Personnel</b>	
Mark Rivers	Co-Director; Research Professor - Tomography
Stephen Sutton	Co-Director; Research Professor- Microprobe
Peter Eng	Research Professor- Interface Diffraction and Optics
Tony Lanzirotti	Research Associate Professor- EXAFS and Microprobe
Matt Newville	Research Associate Professor- EXAFS and Microprobe
Vitali Prakapenka	Research Professor- Diamond Anvil Cell
Sergey Tkachev	Beamline Scientist- Diamond Anvil Cell, Gas Loading System
Joanne Stubbs	Research Associate Professor– Interface Diffraction
Dongzhou Zhang	Beamline Scientist (Univ. of Hawaii)- Diamond Anvil Cell
Yanbin Wang	Research Professor- Multianvil Press
Tony Yu	Beamline Scientist - Multianvil Press
<b>Postdoctoral Scholars</b>	
Feng Shi	Multianvil Press
Timothy Officer	Multianvil Press
Young Jay Ryu	Multianvil Press
Eran Greenberg	Diamond Anvil Cell
TBA	Diamond Anvil Cell
<b>Other Professionals</b>	
Pasquale (Lino) DiDonna	Electronics Engineer (90%)
Nancy Lazarz	Sector Coordinator
Mike Proskey	Mechanical Support and Instrument Design
TBA	Mechanical Support (junior level)
TBA	Software developer
Guy Macha	Mechanical, vacuum support (30%)
Charlie Smith	Computer Systems Administrator (33%)

## 4. Vision

### 4.1. Near-term (1-3 years)

GSECARS is the foremost facility in the world dedicated to earth, environmental and planetary science research using synchrotron radiation. All techniques originally proposed for the sector are operational and available to the general user community during 100% of the available beam time. Our science program is largely driven by the high-impact experiments defined by our users that in turn are driven by funding agency support to these individual investigators. Additionally, our scientific staff has identified the following high-impact core research topics that we intend to emphasize in near-term experiments and technical developments. These topics have been chosen to align with the missions/initiatives/grand challenges of the relevant funding agencies (NSF, DOE, NASA). Our in-house research is being spearheaded by new, targeted funding proposals (with GSECARS senior staff as PIs) that are either awarded, in review, or in preparation, as described below.

#### *4.1.1. Chemical Complexity at Mineral-Fluid Interfaces*

This project seeks to dramatically expand the suite of molecular-level mineral-fluid interfacial structures and solution conditions that can be probed by synchrotron x-ray techniques such as crystal truncation rod (CTR) diffraction and resonant anomalous x-ray reflectivity (RAXR). Expanding the range of minerals and solution conditions that can be probed, and maximizing the speed at which interfacial chemistry questions can be answered, will lead to new, high-level views of mineral-fluid chemical systematics, enabling broad predictive capabilities for adsorption characteristics as well as mineral dissolution and growth mechanisms.

**Award:** Next Generation Synchrotron X-ray Methods and Tools for Quantifying Chemical Complexity at Mineral-Fluid Interfaces; Principal Investigator: J. Stubbs; Department of Energy – Geosciences; \$984,154 (08/15/18 - 08/14/21).

#### *4.1.2. Compositions of Picogram Samples Returned by NASA Spacecraft Missions*

This project will develop and test techniques for applying micro-XAFS and micro-XRD methods to picogram mineral grains focusing on FIB methods for producing mono-mineralic samples. Such capabilities will be crucial in determining the compositions (and therefore chemical and physical histories) of samples returned by NASA spacecraft which are typically characterized by mineral grains with sub-10  $\mu\text{m}$  dimensions.

**Award:** Development of XAFS and XRD Methods Applicable to Picogram Samples Returned by NASA Missions; Principal Investigator: S. Sutton; NASA – Laboratory Analysis of Returned Samples; \$643,000 (02/08/2018 – 02/07/2021). Collaboration with University of New Mexico and University of Nevada – Las Vegas.

#### *4.1.3. Multivalent Element Redox Couples as Oxygen Fugacity Proxies in Igneous Systems*

The aim of this project is to advance the sensitivity, interpretation, and applicability of XAFS data in terms of valence, leading to improved oxygen fugacity determinations. One effort will overcome many of the present limitations by developing and applying high energy-resolution fluorescence detection XAFS (HERFD-XAFS) on the GSECARS X-ray Microprobe using crystal analyzer spectrometers for measuring the fluorescence XAFS. By using high-quality crystals with small lattice spacing, the energy resolution is greatly improved (on the order of  $\sim 1$  eV), which will overcome the signal/background restrictions encountered in XAFS analysis of many natural systems. With energy resolutions smaller than the natural broadening due to the core-hole lifetime, HERFD-XAFS can yield spectroscopic features that are dramatically sharper than those achievable by more conventional TFY-XAFS measurement, facilitating interpretation of subtle differences in valence state and speciation. This system is currently in the design stage. Although other HERFD-XAFS beamlines do exist, they lack microfocusing capabilities and are therefore poorly-suited for analysis of small geologic materials which exhibit fine scale heterogeneity. We

believe this instrument will be unique. A related scientific effort utilizing this new instrumentation will explore changes in copper speciation as a new redox window on metal solubility and transport in magmatic systems.

**In Review:** Collaborative Research: Measurement of Copper Speciation in Basaltic Glasses using X-ray Absorption Spectroscopy, a New Window on Metal Solubility and Transport in Magmatic Systems; Principal Investigator: A. Lanzirotti; NSF – Petrology and Geochemistry; \$87,726 (11/01/2018 – 10/31/2021).

#### ***4.1.4. Extending the multi-anvil pressure range to 50 GPa and beyond***

An initiative titled “*Infrastructural Development for Deep-Earth Large-Volume Experimentation*” (DELVE) received partial support from COMPRES in 2017, to expand pressures beyond 30 GPa in the multi-anvil system. Seven institutions besides GSECARS are involved. Working with users from Case Western Reserve University and University of Hawaii, we have successfully reached 49 GPa at 1800 K, using sintered diamond (SD) as second-stage anvils in DDIA-30. Remarkably, not a single SD anvil has been damaged so far. This demonstrates that 50 GPa experiments at high temperatures can be made routine for users. We are currently working on phase relations in the  $\text{MgSiO}_3\text{-Al}_2\text{O}_3$  system with pressure determination based in-situ x-ray diffraction and plan to produce a phase diagram that may be used as pressure calibration points in laboratories without x-rays.

#### ***4.1.5. Next Generation Tomographic Imaging***

X-ray microtomography is valuable for non-destructively 3D visualization of dynamic processes that occur in porous media during fluid flow experiments, for example. Advances aimed at improved speed, x-ray stability, and pressure/temperature cells for simulating conditions to several km depth will be pursued.

**In Preparation:** Next Generation Synchrotron X-ray Methods and Tools for Tomographic Imaging; Principal Investigator: M. Rivers; Department of Energy – Geosciences; submission anticipated in FY2019.

#### ***4.1.6. Pushing to submicron resolution at 13-ID-E***

The stability of the support table for the microprobe in 13-ID-E has recently been recognized as the limitation to the spatial resolution we can obtain. This will become a much more important factor after the APS upgrade, when we should be able to achieve sub-200nm focal spots. We are in the final stages of designing and ordering a synthetic granite support table to replace the existing steel frame table.

#### ***4.1.7. In-situ laser heated high pressure single crystal diffraction at PX<sup>2</sup>***

*In-situ* laser heated single crystal diffraction at high pressure is not routinely available at any synchrotron facility. At 13-BM-C, the 200W IR laser heating system has been commissioned to carry out laser-heated diffraction at ambient pressure, and for high pressure heat-and-quench diffraction in diamond anvil cells. The next step is to combine the high pressure single crystal diffraction with *in-situ* laser heating, which will require new designs of diamond anvil cells. *In-situ* laser heated high pressure single crystal diffraction with round-table diamond anvil cell has been prototyped in 13-ID-D, and we are working to incorporate this technique in 13-BM-C.

## 4.2. Strategic (3-10 years) and Synchrony with APS Plans

GSECARS is looking forward to the greatly increased brightness with the multi-bend achromat lattice with the APS Upgrade. We requested a number of beamline enhancements to take advantage of this upgrade, and were pleased that the following items for the ID beamlines were identified as Highest Priority and are planned for funding from the APS-U project.

Beamline	Item	Comment	Estimated Cost (K\$)
13-ID-E	Dual, 500 mm horizontal mirrors	Replace or repolish to 100 nrad slope error.	120
13-ID-E	Kirkpatrick-Baez (KB) mirrors (240 mm, 2 sets)	Replace or repolish to 100 nrad slope error.	180
13-ID-E	Double crystal monochromator	Improve thermal and mechanical stability.	50
13-ID-E	End station instrumentation	High stability table	20
13-ID-C/D	1.0 m-long mirrors (one vertical and one horizontal focusing)	Upgrade 100 nrad slope error (repolish or replace)	140
13-ID-C/D	KB system - 350 mm long mirrors	Upgrade 100 nrad slope error, lengthen and bender	200

The principal improvements will be to upgrade optics (mirrors, monochromators) and improve instrument stability to take advantage of the lower emittance likely to be available in 4 years. We will work closely with the APS and our funding agencies to ensure that such beamline improvements will be forthcoming in a timely manner.

One of our concerns about the APS-U is the impact on our bending magnet beamlines. 34% of the publications from GSECARS in 2015-2018 are from the bending magnet beamlines, and this fraction is expected to increase with the new PX2 program on 13-BM-C. With the APS-U the critical energy of the bending magnets decreases, and more importantly it is more difficult to split the bending magnet fan with a clean source (M3 magnet, inboard fan). We will need to move our beamlines and re-design some components to split this inboard M3 fan and work with a smaller separation between the two fans. We look forward to working with the APS to meet these challenges.

APS-U with these beamline enhancements will provide long-term advances to our scientific program, including the following:

### 4.2.1. TeraPascal Studies in the DAC

Diamond anvil cells (DAC) coupled with laser heating techniques are primary tools to study materials at relevant pressure-temperature conditions of planetary interiors. However, the pressure-temperature conditions required to understand the nature and origin of different planetary systems are either very difficult to reach (Earth's core-mantle boundary and core, >130 GPa and >4000K) or lay beyond typical experimental limits (gas giants and exoplanets, >400 GPa and >6000K). A recent breakthrough with the development of the double stage anvil technique, successfully tested at GSECARS, has the potential for studying materials *in-situ* at pressures above 1 TPa. For these experiments, opaque nanocrystalline diamond micro-balls were used as secondary anvils to compress samples at room temperature. To combine this technique with laser heating optically transparent anvils will be utilized, made possible now with recent improvements in the synthesis of transparent nano-diamond micro-balls or by using single-crystal or polycrystalline micro-anvils shaped with FIB. Thus, dramatically extended (more than three times) pressure-temperature conditions far beyond typical DAC experiments will be generated to probe mineral properties using high-resolution, synchrotron x-ray techniques providing insight on long standing questions concerning the origin, structure, thermal state and internal dynamics of various planetary systems. The APS-U with the enhancements described above will give us a greater flux into a smaller spot revolutionizing

in-situ XRD high-pressure studies and increasing the feasibility of expanding the accessible pressure range to 1 TPa and beyond.

APS-U and beamline enhancements will also allow multi-phase experiments to be conducted with both DAC and multi-anvil press high-PT devices (13-ID-D), thus positioning us at the forefront of beamline capabilities in the world. For in-situ diffraction studies at such pressure conditions, a tightly collimated white beam is required to obtain structure and composition information from the sample, with minimum contamination from the surrounding solid pressure media. Deformation experiments in the press will provide important information on rheology under these conditions; a bright mono source with energies up to 80 keV is required, so that useable d-spacing can be “compressed” within a limited solid angle of 6-7 degrees.

#### ***4.2.2. Spatial Resolution and Element Sensitivity Advances for Microspectroscopy***

These upgrades will allow fundamentally new types of microscopy studies at 13-ID-E. For example, a large fraction of the current 13-ID-E users are conducting valence state  $\mu$ XAFS measurements of mineral phases and glasses to infer the oxidation states of the environments from which they formed. Many of the most interesting and relevant specimens for understanding the evolution of the early solar system are below the micron scale, which currently cannot be studied at 13-ID-E. Similarly, there is a large community of environmental scientists seeking to understand the biogeochemical controls on the heterogeneous reactivity of elements at mineral-fluid interfaces. At our current spatial resolution of 1-2  $\mu$ m, it is challenging to precisely evaluate changes in molecular speciation along such interfaces, this requires stable spectroscopic analysis at the 250 nm scale. There are also new opportunities for understanding controls on chemical incorporation in colloids, on atmospheric particles, and within micro-organisms. Some of the most abundant marine organisms in tropical and sub-tropical oceans, whose activity is known to impact oceanic and atmospheric elemental cycles, are at the scale of 500 nm, too small to be effectively analyzed with current capabilities. The causes and treatment of respiratory diseases associated with the inhalation of fine particulate matter is another research area of potentially high societal impact. With the ability to conduct XAFS at spatial resolutions of 250 nm, the speciation of individual  $PM_{2.5}$  particles (those with size  $\leq 2.5$   $\mu$ m that can penetrate deeper into the lungs and are of the greatest health concern) can be evaluated to establish interactions with tissue to form potentially toxic species.

#### ***4.2.3. Interface Science Advances***

The 13-ID-C interface science program will be advanced by expanding the suite of accessible minerals and making Bragg Coherent Diffractive Imaging (BCDI) feasible. 13-ID-C currently offers two primary classes of techniques: (1) surface and interface scattering (both resonant and non-resonant) such as crystal truncation rod (CTR) diffraction and resonant anomalous x-ray reflectivity (RAXR) to determine atomic-level interfacial structures and adsorbate positions; and (2) Grazing incidence (GI) methods including GI-XAS and long-period standing wave fluorescence yield (LPSW-FY) which are laterally averaged but have inherent nanometer-scale resolution in the surface-normal dimension. Experiments in the first class require multi-axis diffractometry, and have been limited to single crystals  $\sim$ millimeters in lateral extent. The technique will have far more scientific impact when the proposed enhancements allow applications to smaller crystals, as many important minerals are “size-challenged”. Measurements on crystals  $< 300$   $\mu$ m are currently limited by low signal and our inability to keep the crystals well-centered in the x-ray beam with existing instrumentation. APS-U will benefit these experiments and the beamline optics enhancements will provide focusing mirrors that will preserve the brightness of the source. The diffractometer will also need to be upgraded to maintain coincidence between sample and beam during multi-axis rotation. The second (GI) class of techniques will also benefit from diffractometer upgrades. BCDI will allow us to bring to the broad geoscience community the opportunity to investigate strain within nanocrystals and study the manner in which the presence of adsorbate species influences the underlying crystal structures.

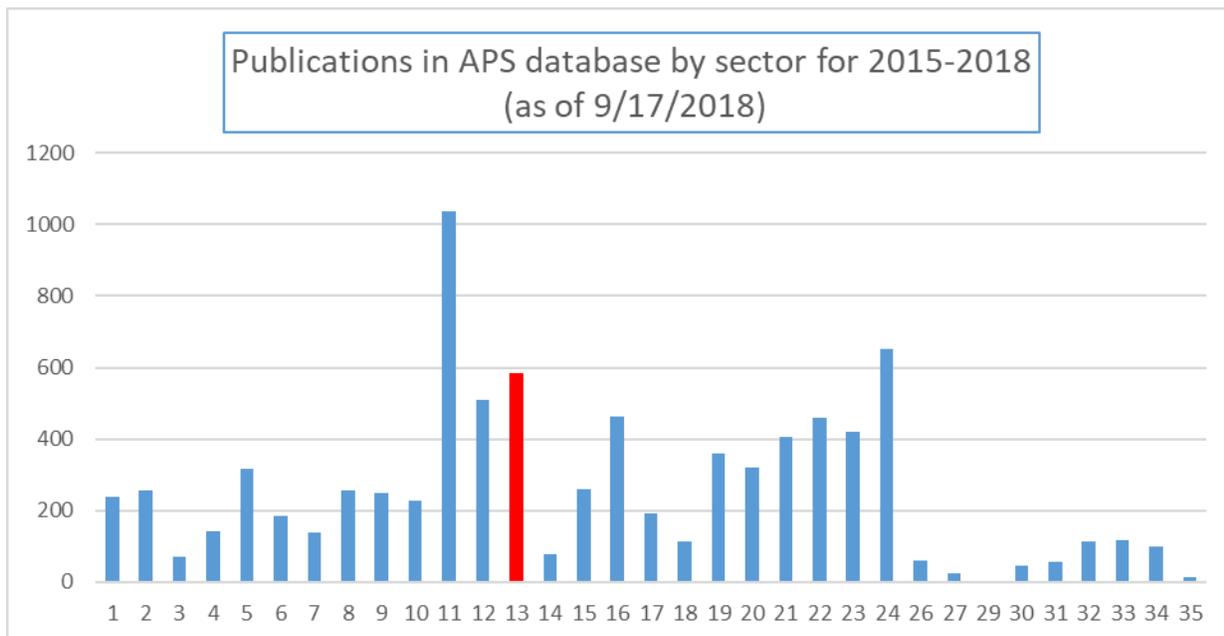
## 5. Funding

Prior to 2018 GSECARS was supported primarily by two operations grants: one from NSF-Earth Sciences (~2/3) and the other from DOE-Geosciences (~1/3). We applied for a 5-year renewal of both of these awards in 2016. The NSF award was renewed at the requested level. However, DOE-Geosciences decided to phase out facility support for GSECARS, with reduced funding of \$700K in 2017 and 2018, and then no funding after that. DOE-Geosciences is receptive to proposals that focus on technique development or science applications, and has indicated that it may be able to fund three such awards, each at the \$300K/year level. They requested staggered submissions with one each in 2018, 2019, and 2020. We were successful in our 2018 submission entitled “*Next Generation Synchrotron X-ray Methods and Tools for Quantifying Chemical Complexity at Mineral-Fluid Interfaces*” (Joanne Stubbs, PI). This award is labelled “DOE surface” in the table below. We intend to submit the second of these DOE-Geosciences proposals for tomography development in 2019. Because GSECARS makes many contributions to the APS outside of sector 13 (optics, software, etc.), we have also approached the APS about providing funding for GSECARS to make up for the loss of facility operations support from DOE-Geosciences. They have been receptive to this request, but no final decisions have been made pending the FY19 APS budget, and the fate of our pending proposals. In the following table entries in italics are planned submissions, others are existing awards. The funding in future years for existing awards is subject to change depending on agency funding levels.

<b>Sector 13 GSECARS Funding Profile (thousands \$)</b>					
<b>Funding Source</b>	<b>FY2016 (2 years prior)</b>	<b>FY2017 (Previous Year)</b>	<b>FY2018 (Current Year)</b>	<b>FY2019 (Next Year)</b>	<b>FY2020 (2 Years Out)</b>
<b>NSF operations</b>	\$2,652	\$2,785	\$2,587	\$2,974	\$3,037
<b>DOE operations</b>	\$866	\$700	\$700		
<b>COMPRES gas loading</b>	\$56	\$58	\$58	\$58	\$58
<b>COMPRES PX2</b>	\$150	\$150	\$276	\$150	\$150
<b>DOE surface</b>				\$320	\$321
<b>DOE tomography</b>				<i>\$300</i>	<i>\$300</i>
<b>NSF plastic deformation</b>	\$120				
<b>NSF silicate liquids</b>	\$112	\$112	\$112		
<b>NSF high-pressure faulting</b>		\$125	\$125	\$125	
<b>NSF Larch</b>	\$135	\$135	\$135	\$135	
<b>NASA LARS</b>			\$344	\$142	\$145
<b>TOTAL</b>	\$4,091	\$4,065	\$4,337	\$4,204	\$4,011
<b>Comments</b>			Includes \$326 in one-time capital equipment from LARS and PX2		
<b>Projected Funding Needed to Achieve Short Term Vision (Total Costs)</b>	NA	NA	NA	\$4,200	\$4,200

## 6. Self-Assessment

*Publications:* GSECARS has been very successful in terms of productivity (publications, etc.) and attracting users to the facility. The following plot shows the number of publications in the APS Publication Database for 2015-2018 by sector. GSECARS (highlighted in red) has the third most publications of all sectors with 585. Only sector 11 with the mail-in powder diffraction program and the sector 24 (GMCA) macro-molecular crystallography program have more publications in this time period, with 1038 and 650 publications, respectively.



*Staffing:* Our success is due in part to the fact that we are funded at a sufficiently high level to be able to hire sufficient numbers of highly skilled personnel including scientific, technical, and administrative staff. GSECARS has more personnel than most other sectors at the APS, however, we also provide a large number of state-of-the-art capabilities utilizing seven principal instruments in five experimental stations, four of which operate simultaneously. Thus, our “scientific and technical staff per instrument” value is near two, a common level for a synchrotron facility. We view the key to our success being the fact that GSECARS beamline scientists are (1) knowledgeable of the science, (2) knowledgeable of the instrumentation and techniques, (3) interested in collaborating with other investigators, and (4) skilled in assisting novices.

*Canted Undulator Upgrade:* With the successful completion of our canted undulator upgrade in 2013, the GSECARS sector can now run four simultaneous experiments (2 ID, 2 BM) allowing a high level of productivity. This extensive array of instruments allows us to conduct essentially any X-ray measurement that is of interest to the earth, environmental and planetary science community.

*X-ray Microprobe:* Our upgraded microprobe beamline is most likely unique in the world in allowing absorption edge studies between 2.3 and 28 keV. Thus, sulfur K and antimony K XAFS measurements can be done nearly simultaneously on the same spot on a sample. Most other microprobes are designed to access either tender (1-5 keV) or high-energy (>5 keV) but not both.

*Diamond Anvil Cell.* The laser heated DAC facility in 13-ID-D is viewed by many as the best in the world. We provide a double-sided laser heating system with Yb-fiber lasers and a beam shaper that allows us to control the beam size independent of the power, to achieve a large flat-top heating spot. A CO<sub>2</sub> laser heating system (COMPRES funded) was added, making this a very versatile apparatus for research in the DAC. A unique online Brillouin spectroscopy system (co-funded by COMPRES) in the 13-BM-D station

provides *in-situ* elasticity studies for materials at extreme conditions. With this system, it is possible to measure sound velocities and densities of materials simultaneously, resulting in an absolute pressure scale and determinations of important material properties (e.g., equations of state and elasticity) as a function of pressure and temperature. High resolution X-ray diffraction and Brillouin spectroscopy collected simultaneously from the same sample area and in the same pressure-temperature environment provide information essential for interpreting seismic observations and constraining models of the composition and evolution of the Earth.

*Multi-anvil Press:* The 1000 ton press in 13-ID-D is a unique, X-ray accessible, multi-anvil press. We have developed novel techniques including the deformation DIA (DDIA) and the rotating anvil apparatus (RAA). Both modules were designed and engineered at GSECARS. The DDIA has now been used at other laboratories. The RAA allows imaging sample microstructure using computed microtomography at high pressure. We also provide capabilities for *in-situ* ultrasonic velocity measurements and acoustic emission measurements.

*Surface and Interface Diffraction:* These experiments utilize state-of-the-art Pilatus pixel-array detectors which speed up data collection by a factor of 10 or more over previous generation point detectors. Unique to these instruments is the availability of an in-house designed (P. Eng), *in situ* gas and liquid cell for radioactive material and atmosphere-sensitive interface studies. The cell consists of multiple containment layers which satisfy radiation safety requirements and shield crystal surfaces against air exposure. Remote liquid control is fully contained and the containment domes are fully X-ray-scattering compatible allowing measurements to be done in variable composition atmospheres and aqueous solutions. We have recently developed methods for measuring interfacial structures from crystals measuring as small as 100  $\mu\text{m}$ , an order of magnitude smaller than previous studies which were limited to crystals  $> 1 \text{ mm}$ .

*Microtomography:* The microtomography program is complementary to the dedicated system at beamline 2-BM. 2-BM does not provide monochromatic photons above 28 keV, whereas most studies at 13-BM are in the energy range of 30–40 keV. In particular a large fraction of our users are studying fluids in porous media using differential absorption tomography at the iodine (33.169 keV) and cesium (35.985) K absorption edges. We have recently added capabilities for fast tomography using pink-beam for dynamic studies of fluid flow. We have achieved data collection times under 10 seconds for a complete 3-D data set.

*Gas-Loading Apparatus for DACs:* We have designed and constructed a unique system for loading gases at high pressure into diamond anvil cells at pressures up to 200 MPa (co-funded by COMPRES). The gases are used either as a quasi-hydrostatic pressure media surrounding the sample, or as the sample itself. The diamond cell is sealed using a clamping mechanism, which permits nearly any type of diamond anvil cell to be used. Online ruby fluorescence and video imaging systems allow *in-situ* monitoring of the pressure and gasket deformation as the cell is sealed, resulting in a very high success rate in loading cells. Last year this system loaded 751 diamond cells, of which 466 were used at beamlines other than GSECARS.

*Contributions to the Community:* GSECARS has pioneered developments in a number of technical fields, and has worked to share these developments with other beamlines at the APS and elsewhere.

GSECARS has collaborated with other groups at the APS in the development of a sophisticated beamline control and data acquisition system called EPICS. This is an extensible, distributed control system based on real-time controllers and user interface software running on Windows, Mac, and Unix. The EPICS software for beamline control is called synApps, and is distributed by the Beamline Controls and Data Acquisition (BCDA) group at the APS. Over 50% of the software in this distribution is written and maintained by Mark Rivers from GSECARS. This includes the areaDetector software installed on most 2-D detectors at the APS. areaDetector is used across the DOE user facilities, including NSLS-II, SNS, and LCLS. The user community benefits greatly from having facilities using the same software, since there is only one system to learn. It is also more efficient, since development costs are reduced.

In order to focus the APS source to a few microns, Peter Eng from GSECARS developed a pair of very asymmetric elliptical Kirkpatrick-Baez mirrors. This achromatic optic can be used to focus either white or monochromatic X-rays, and resides in the experimental station close to the sample. A scalable bender mechanism was developed, and was made available to other institutions through the University of

Chicago machine shop. An enhanced version of this design is now being sold commercially by IDT. The large, water-cooled Kirkpatrick-Baez mirrors in 13-ID-B and C were designed and constructed by GSECARS. This design is also being sold commercially by IDT and these are installed at HP-CAT and DCS at the APS, the Swiss Light Source, the Canadian Light Source, the Australian Synchrotron, and Diamond. Peter collaborated with IDT on the design of an air-bearing monochromator, with the initial installation on 13-ID-E. This design is now installed on 10-ID and 9-BM at the APS as well.

GSECARS staff perform important duties in the community including serving as members of APS Proposal Review Panels, chair of the APS Partner User Committee, previous chairs of the APSUO, etc.

The principal threat to the success of GSECARS is the funding uncertainty associated with federal agency budget reductions. For example, the loss of DOE Geosciences facility support has made us more dependent on smaller, short-term awards, each of which has a chance of not being funded over the long term.