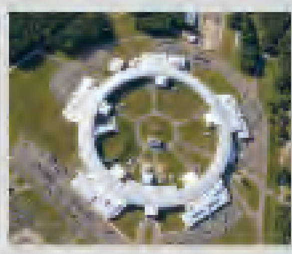

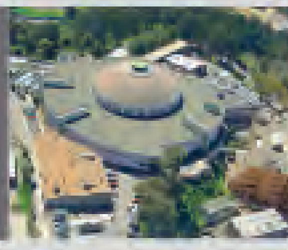
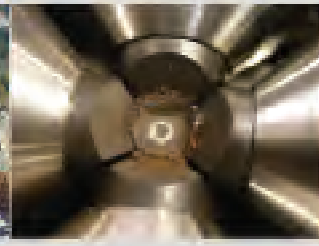
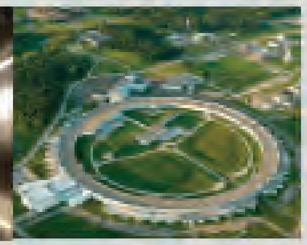

COMPRES

The Consortium For Materials Properties Research in Earth Sciences (IV)
National Facilities and Infrastructure Development for High-Pressure Geosciences Research

Proposal to NSF 2017-2022

APPENDIX A



APPENDIX A:

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COMPRES Facilities

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COMPRES Facilities

1. ALS 12.2.2 Beamline DAC (PI: Quentin Williams, UC Santa Cruz)

Over the next five years, we plan to continue to augment the portfolio of the Earth Sciences high-pressure effort at the Lawrence Berkeley National Labs Advanced Light Source, while continuing to maintain the standard capabilities that have served our user community well. Specifically, we will complete the development of our recently operational high-pressure single-crystal diffraction system, with a particular focus on simultaneous high-pressure and external heating capabilities. At the same time, we will maintain and augment the developments that we have made in radial diffraction and external heating, while continuing to enable standard high-pressure polycrystalline x-ray diffraction, both at ambient temperatures and under laser heating. Our net goal is to continue our facility's capabilities at interrogating materials at pressures and temperatures spanning those present in the upper mantle, transition zone, and lower mantle, with high-precision single crystal measurements being feasible at pressures and temperatures spanning those within subduction zones, and pressures that access those found throughout the silicate portion of the Earth. We will continue to pursue a greater level of interaction between our primary diffraction (with laser-heating) beamline (beamline 12.2.2) and the highly complementary microdiffraction capabilities of the neighboring 12.3.2 beamline, as well as the infrared beamline 1.4.4 that has recently been reconfigured to enable high-pressure infrared measurements. Automation of pressure and temperature controls and spatial mapping as well as designing our infrastructure for ease of use for better efficiency and remote operation are, and will continue to be, operational themes for beamline use. As a user-friendly facility, the excellent sample preparation facilities that were put on-line over the course of COMPRES III—including a state-of-the-art laser milling set-up, a gas-loading apparatus and a redesigned sample preparation laboratory—will be sustained on an ongoing basis for users (and augmented as requested, and as our budget allows). To accomplish these goals, and continue to provide state-of-the-art service to users, we request over the course of COMPRES IV: continued support for two beamline scientists; funding for expendable materials; and a new sample preparation microscope (as overused sample preparation equipment requires replacement). Among these, the support for the beamline scientists, whose three-fold goals are user-support, development of new capabilities, and pursuing their own (or a collaborative) scientific agenda, is critical for the ability of 12.2.2 to ensure that users are as productive as possible while utilizing state-of-the-art, well-maintained equipment. Furthermore, the COMPRES support has leveraged very substantial contributions from the ALS/DOE to both infrastructure/equipment and staffing in direct support of high-pressure science at beamline 12.2.2: this is a major supplementary benefit to the geosciences community of COMPRES support at the Advanced Light Source.

High-Pressure Facilities/Capabilities and Future Plans at the Advanced Light Source
Beamline 12.2.2 is an extreme conditions beamline at the Advanced Light Source (ALS), a 1.9 GeV 3rd generation synchrotron light source. This beamline utilizes a 5.3 Tesla superconducting bending magnet as the source for a continuous spectrum, with a critical energy of 12.7 keV and useable X-ray photons from ~ 5 keV to ~ 40 keV. There are two endstations on this beamline, of which endstation 1 had not been deployed until this year. COMPRES-ALS has, in collaboration with ALS staff, now done a full redesign of endstation 1 and oriented it towards single-crystal x-ray diffraction measurements. A new (as of 3/16) Stoe Stadi-Vari 4-circle Eulerian cradle

diffractometer coupled to a fast CMOS detector has been mounted on this endstation. The diffractometer has both a customized rugged sample carrying ability, and also a small sphere of confusion: this apparatus is both engineered for high-pressure samples, and neatly exploits the source characteristic of ALS beamline 12.2.2. The diffractometer and detector were purchased from ALS/DOE funds following proposals and negotiation with ALS management. COMPRES-III contributed mounting motors and stages to enable precision alignment of the single crystal diffractometer on beamline 12.2.2, as well as an adjustable collimator system to give users the flexibility to choose the beam size for their single crystal experiment. The net breakdown was that COMPRES funds were leveraged for this new community capability at roughly a 4:1 ratio (4 ALS/DOE:1 COMPRES). Notably, the presence on-the-floor of COMPRES staff with strong single crystal expertise was critical for negotiating the launching of this new facility. The diffractometer is deployed and collecting high-pressure single-crystal data; we are currently optimizing the system and set-up to enable routine simultaneous external heating of pressurized single-crystal samples. On endstation 2, which comprised the primary 12.2.2 beamline until the deployment of the single-crystal set-up, a double-sided laser-heating and spectroradiometry setup and an in-hutch ruby fluorescence system are available for pressure characterization. Either a MAR345 image-plate system or a Bruker P200 CCD are deployed for x-ray detection (made available by the ALS), and either axial or radial diffraction studies can be carried out on endstation 2.

The Advanced Light Source (in tandem with COMPRES) has provided key infrastructure for high-pressure Earth Sciences research for a broad range of national and international investigators: the appendices to this proposal describe in detail our user base, publication output, and amount of time allocated to COMPRES users. While the "core" COMPRES user-base of 12.2.2 is from the Western U.S., a region with a long-standing and vibrant high-pressure community within the Earth Sciences, the ALS capabilities have attracted a global clientele in our particular areas of focus. From an operational standpoint, the Approved Program (AP) arrangement of COMPRES with the Advanced Light Source (which currently extends from Jan 2015- Dec 2018) guarantees that at least 35% of the beamtime at 12.2.2 be allocated to COMPRES users. Operationally, ALS and COMPRES have agreed that all user time at 12.2.2 is allocated through the ALS General User program. This has resulted in between 55 and 78% (varying depending on the 6-month cycle) of the available user time at 12.2.2 being allocated to COMPRES-affiliated users, with the balance being primarily to materials scientists. Obviously, these usage rates are far in excess of the 35% formal allocation, and COMPRES has hence never had to invoke the AP minimum guarantees on COMPRES user time. That the COMPRES user base has been so successful in the General User program is a manifestation of both the caliber of proposals for time from the COMPRES community, and the substantial user base of 12.2.2 within the geosciences community.

Over the course of COMPRES-III, the ALS 12.2.2 COMPRES effort has included improvements such as having: (1) fully redesigned, rebuilt and redeployed our high-pressure laser-heating set-up so that it is a stable, user-friendly, state-of-the-art synchrotron laser-heating apparatus (this complete redesign/rebuild was funded by the ALS); (2) launched a dedicated, state-of-the-art high-pressure single-crystal diffraction set-up, which is currently under active development (this has been funded at the ~80% level by the ALS, with an upcoming ~20% contribution for supporting equipment—stepper motors, collimators, etc.---from COMPRES); and (3) augmented our capabilities in external heating, radial diffraction and dramatically improved our sample preparation capabilities. These sample preparation capabilities include a Chicago-manufactured gas-loading apparatus (paid for by the ALS during the COMPRES III period), and a high-quality laser-miller (funded from COMPRES ARRA funds). Our net goals have been to provide a user-friendly facility that can allow users to accomplish a broad suite of measurements, from comparatively routine high-pressure diffraction measurements, to more challenging areas in which the interests of our user base coupled with our on-site expertise have led us to focus.

In short, COMPRES funding has resulted in a flourishing facility for high pressure Earth Sciences synchrotron work on the West Coast.

COMPRES funding has provided key support that has leveraged not only infrastructure and beamtime, but also extremely significant personnel resources from the Advanced Light Source itself. In particular, the ALS has provided both staffing and extensive infrastructure in addition to that provided by COMPRES for high-pressure beamline 12.2.2: senior beamline manager Alastair MacDowell was assigned to 12.2.2 for much of the past five years (initially at 50%, later at 33% time), and has been replaced in most managerial roles by Martin Kunz (who has extensive Earth Sciences/high-pressure expertise), although MacDowell remains available on a consultative basis (see Figure 1). From a technical support standpoint, Andrew Doran (75% time at 12.2.2) provides trouble-shooting and user support beyond those supplied by the COMPRES technical support. Indeed, the expertise of Kunz/MacDowell and Doran provide an extremely valuable complement/match to the COMPRES-funded employees. In short, the West Coast COMPRES enterprise has engaged in a highly successful partnership with the ALS: one that has produced both high levels of staffing and equipment infrastructure, each of which are directed towards generating productive user experiences. So, in net, the COMPRES personnel support is completely integrated with the ALS support that it helps to leverage: and the combination of COMPRES-funded and ALS-funded personnel have generated a well-staffed, user-friendly beamline.

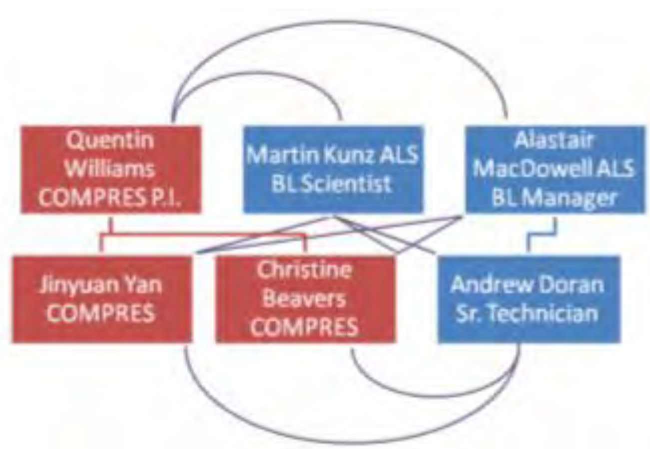

Figure 1. Our current beamline management structure, with COMPRES-affiliated staff in red and ALS staff in blue. Purple lines indicate advisory interactions. COMPRES staff report to Williams, Kunz reports to ESG group leader Howard Padmore (not in org. chart), and Doran reports to MacDowell.

The ALS has contributed VERY substantial staffing, equipment and infrastructure support that has greatly benefited the COMPRES user-base, and which has been leveraged by COMPRES.

Towards the start of the upcoming five-year period, we have positioned ourselves to couple single-crystal x-ray diffraction with our long-standing expertise in external heating (e.g., Miyagi et al., Rev. Sci. Instrum., 84, 025118, 2013) to *routinely* monitor the crystal structures of a range of geologic materials across a range of pressure/temperature conditions. Single crystal diffraction is, of course, the premier technique for deriving accurate atomic positions and displacements, and can monitor phenomena that impact physical and thermoelastic properties such as disorder and internal structural shifts/deformations within unit cells. It also is critical for illuminating the relative structural changes induced by pressure and temperature in materials. Thus, while we certainly plan to continue our support for polycrystalline diffraction, our sense is that the COMPRES community will progressively make a transition towards greater usage of single-crystal measurements--particularly as polycrystalline measurements on major Earth components increasingly run their course. In this respect, we anticipate that the first two years of the COMPRES IV grant (and moving forward) will involve an emphasis on pushing our user community towards tandem usage of 12.2.2 and of the Laue microdiffraction capabilities at 12.3.2. We expect that this will, given the expertise of Kunz and Beavers, be a particularly fruitful direction, probing the interface between polycrystalline and single-crystal measurements. Preliminary tandem experiments at 12.2.2 and 12.3.2 (e.g., Friedrich et al., PRL, 105, 085504, 2010) were demanding and heroic (but also scientifically fruitful)---one of our goals, as we establish our single-crystal facility, is to make the interface between 12.2.2 and 12.3.2 both more user-friendly and much more widely known, and appreciated, among our user community. The scientific motivations for this interaction is simple: synthesis and high P/T characterization of samples can be conducted at 12.2.2, followed by detailed chemical and structural imaging of the quench products at 12.3.2. In short, structural characterization of single-grains embedded within/synthesized in polycrystalline aggregates has become a widely recognized future direction for the high-pressure community: but it does continue to be practiced primarily by specialist practitioners, and we believe that the ALS, both because of inter-beamline cooperation/scheduling and proximity, represents an ideal venue for making such measurements a routine part of the high-pressure experimentalists' toolbox.

A Few Examples of Scientific Highlights Illustrating Capabilities and Future Directions at 12.2.2

Here, we briefly present four examples of studies conducted at 12.2.2 that combine illustrations of either our technical capabilities or developments during COMPRES-III. The four examples are (1) associated with radial diffraction (and hence measurements of preferred orientation and strength) under pressure, (2) advances made in association with our laser-heating and temperature measurement system, (3) recent results from our new high-pressure single-crystal facility, and (4) a description of our extension of external heating capabilities in the diamond anvil cell to temperatures substantially higher than those previously achieved. Our intent here is not to provide a comprehensive portrait of the science conducted to date under the aegis of COMPRES-III at 12.2.2 (which includes an extensive number of studies on standard, 300 K axial diamond cell x-ray diffraction equation of state measurements). Rather, we choose these because they either illustrate technical achievements of the type we believe will continue at ALS under COMPRES-IV, or they illustrate capabilities (like radial diffraction) in which the

COMPRES effort at ALS represents a premiere facility, or in which we fully anticipate COMPRES at ALS will provide a premiere facility during COMPRES-IV (like single-crystal diffraction).

The 12.2.2 facility continues to be a leader in state-of-the-art radial diffraction within the diamond anvil cell, as shown, for example, Marquardt and Miyagi (Nature Geosci., 8, 311–314, **2015,** Figure 2 below.). Their careful examination of the deformation behavior of (Mg,Fe)O ferropericlase, using radial diffraction on beamline 12.2.2, indicates that a substantial viscosity increase in this material may be responsible for the slab stagnation within the shallow lower mantle that has been observed in a range of subduction zones with seismic imaging. Specifically, in high strain regions where ferropericlase is anticipated to be interconnected, the substantial increase in strength (and hence viscosity) occurring between 20 and 65 GPa is anticipated to impede slab penetration; at deeper depths, weakening associated with the spin transition of iron may generate a viscosity structure that is peaked in the shallower lower mantle. Previous studies to examine this behavior had not employed radial, angle dispersive techniques, and therefore had been blind to the texture and strain development in this system. This type of radial diffraction study has been a major focus of 12.2.2 through COMPRES-II and –III. As we discuss below, we fully anticipate that our notable developments in external heating and combined external heating and laser-heating will enable a sequence of rheological studies at 12.2.2 at simultaneous pressure and temperature conditions: as such, we fully expect that ALS will be a primary player in constraining the rheology of Earth’s lower mantle at realistic pressure and temperature conditions over the course of COMPRES-IV.

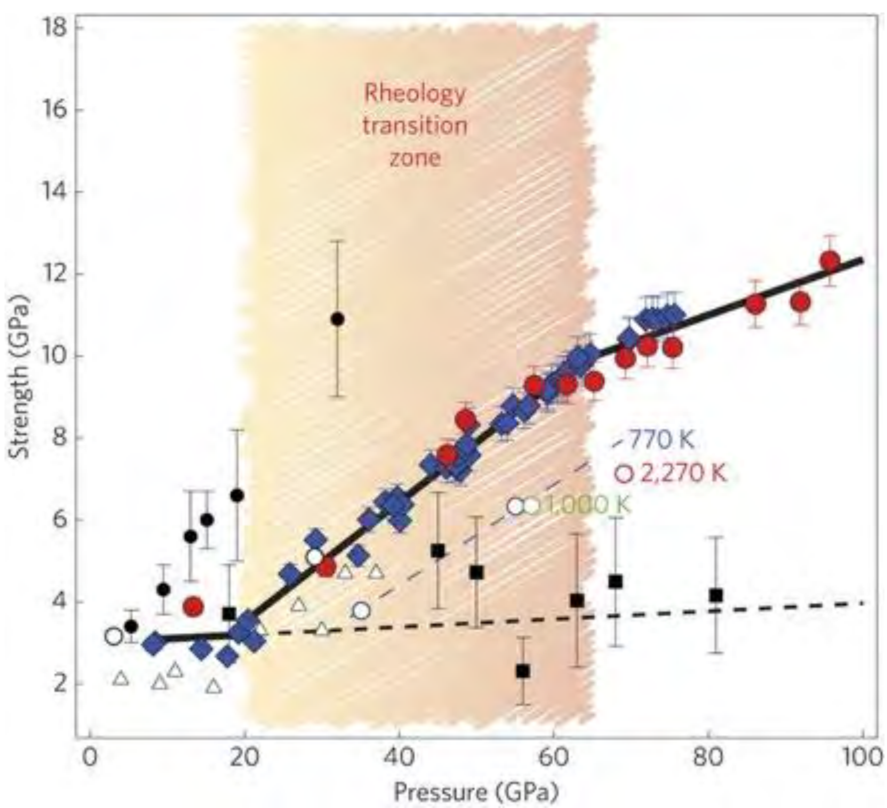

Figure 2: Red circles & blue diamonds, new measurements from Marquardt and Miyagi (2015) at 12.2.2. Solid black lines, linear fits to data in the pressure ranges <20 GPa, 20–65 GPa and >65 GPa. Dashed black line, linear extrapolation of data at pressures <20 GPa. Black squares, $(Mg_{0.83}Fe_{0.17})O$ (Lin et al., PCM, 2009), White triangles, $(Mg_{0.4}Fe_{0.6})O$ (Tommaseo et al., PCM, 2006). White circles, blue dashed line, $(Mg_{0.8}Fe_{0.2})O$ (Miyagi et al., RSI, 2013). Black circles, $(Mg_{0.9}Fe_{0.1})SiO_3$ bridgmanite (Merkel et al., EPSL, 2003).

Second, as an illustration of our role as a community facility whose reach extends beyond simply supplying users with x-rays (and skilled help, and preparation facilities, and infrastructure, and often supplies), we note that our laser-heating system and its associated spectroradiometric temperature measurement system, which were completely redesigned and rebuilt in 2014, are optimized tools to monitor and characterize temperature gradients within the diamond anvil cell (Figure 3). This highlight is chosen because we believe that it amply illustrates the very high caliber of our experimental infrastructure associated with laser-heating. Moreover, it demonstrates that one of the primary 12.2.2 tasks proposed to be accomplished in COMPRES-III, to establish our laser-heating system as a premiere, user-friendly facility, was successful. In particular, the ability to accurately characterize not only average temperatures, as in Figure 3a, but also to accurately characterize temperature gradients rapidly and reliably (Figure 3c) is a critical aspect of both making reliable high-pressure/high-temperature equation of state measurements and conducting accurate phase equilibria measurements in the diamond anvil cell. That our laser-heating system has been used for proof-of-concept experiments for algorithms for inversion of temperature gradients in the diamond cell indicates its utility as a facility and community resource.

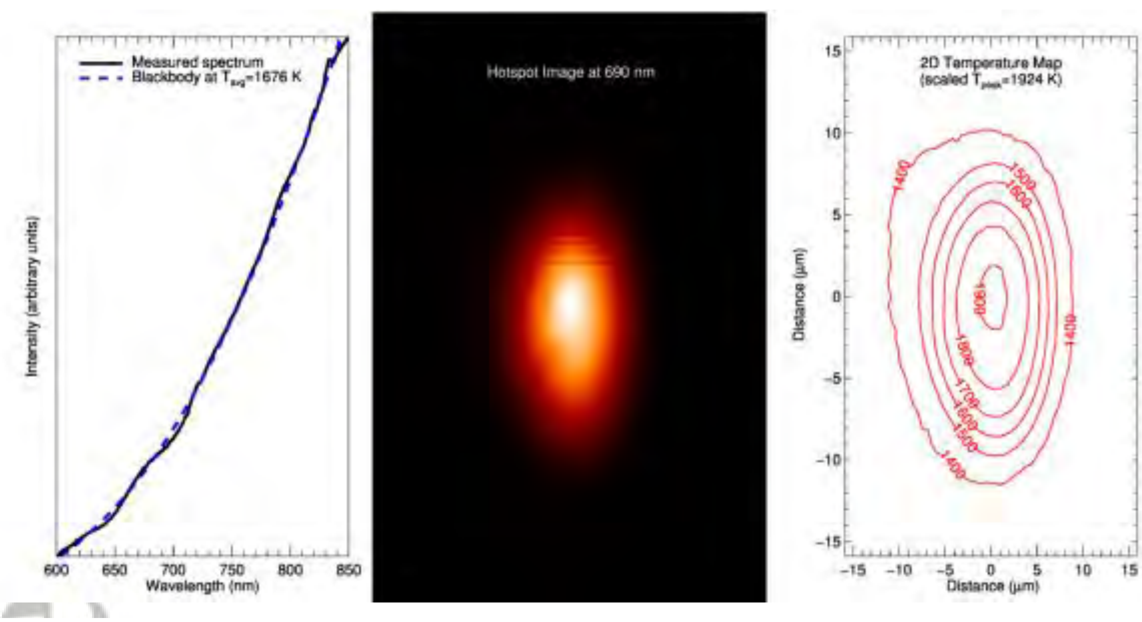

Figure 3. Measurement of a 2-D radial temperature distribution in AgI laser-heated at 17.2 GPa in the diamond anvil cell. From Rainey and Kavner, JGR, 2014 (doi: 10.1002/2014JB011267). At left (a) is a spectrum (with fit: blue dotted line) at an average T of 1676 K (black line is observations, blue dotted line is the Planck grey-body fit); center (b) shows the intensity distribution within the laser-heated hot spot at 690 nm; and the right shows the inverted temperature distribution for the laser-heated spot (note that the y-axis scale is larger than the x-axis scale in both (a) and (b)).

Third, our new high-pressure single-crystal capabilities are illustrated by our very recent results on lawsonite $CaAl_2Si_2O_7(OH)_2 \cdot H_2O$ (O'Bannon, Beavers and Williams, GRL,submitted). This hydrous phase is an important water reservoir in subducting oceanic crust, and is a significant carrier of water to depths greater than ~150 km. As an initial shakedown project on our new single-crystal diffraction system, we conducted high-pressure synchrotron-based single-crystal x-ray diffraction experiments at room temperature up to ~12 GPa to study its high-pressure polymorphism. It has been known for some time that lawsonite converts to a high-pressure phase near 9 GPa, and the structure of this high-pressure phase had not yet been solved using single-crystal diffraction. We utilized the new single-crystal system at the ALS to solve this structure. Above ~9.0 GPa, lawsonite can be indexed to a monoclinic unit cell with $P2_1/m$ symmetry. The distortion of the Ca site increases across this transition, and the single Al site becomes two unique sites in the high-pressure phase. Most importantly for the retention of water within this structure, the hydrogens associated with the hydroxyl group in this structure appear to become disordered across this transition, with implications for both the dehydration mechanism, hydrogen mobility, and electrical conductivity of lawsonite in its high-pressure phase. The key aspect of this illustration is simply that it demonstrates that our newly-set-up single crystal x-ray diffraction set-up is not only capable of high-pressure single-crystal measurements, but that our in-house equipment and expertise is capable of solving high-pressure structures that have proved challenging for the community.

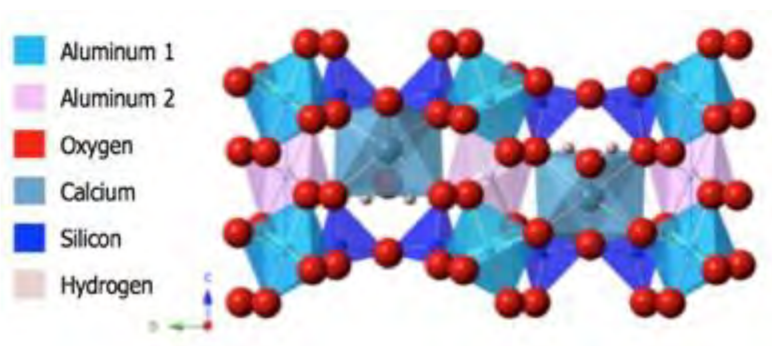

Figure 4. The 9.7 GPa crystal structure of the high-pressure phase of lawsonite looking down the *a*-axis, as refined from single-crystal data at 12.2.2. Note the two unique Al-sites are shown in different colors. The disordered hydroxyl units, which reside at the edges of the Al-octahedra, are not shown in this projection.

Fourth, recent developments using a modified Liermann-type diamond anvil cell at the Advanced Light Source have resulted in the shattering of past records for the pressure and temperature range of externally heated diamond anvil cell work (Figure 5: Miyagi et al. 2013). The pressure/temperature range that was accessed (40 GPa, 2000 K) in a radial diffraction experiment was achieved in an assembly that was designed to impede the kinetics of the diamond reversion reaction through generation of a highly reduced environment immediately adjoining the diamond anvils. While the deformational information produced in these experiments on iron alloys is of substantial value, from a facility perspective, the more important aspects of these experiments are (1) that we now have external heating capabilities that bridge the "thermal gap" between externally-heated diamond cell experiments and laser-heated experiments (which typically become difficult to measure/conduct at temperatures below ~1500 K), and (2) that we also have the ability to simultaneously laser-heat externally heated samples (Miyagi et al., 2013). This latter capability has the prospect of producing substantially larger and lower thermal gradient laser-heated spots: a capability for which the ALS set-up is well-suited and for which preliminary results look promising. Indeed, as Figure 4 shows, temperature gradients of 50 K/□m are routine in laser-heated diamond anvil cell experiments (with larger gradients being present in higher-temperature experiments). These gradients render accurate phase equilibria measurements challenging, and geochemical partitioning experiments uncertain for static pressure conditions that can only be routinely accessed in the diamond cell: or, those that span the pressure range of the deep lower mantle and core. Our targets moving forward include miniaturization and optimization of the external-heating techniques shown in Figure 5. In short, the ALS facility has pushed external-heating technologies in the diamond anvil cell to their current limit, and we expect not only that these capabilities will continue to serve our user community through COMPRES-IV. As importantly, our external-heating techniques, when fully deployed in combination with our single-crystal diffraction capabilities and our laser-heating/temperature-measurement system are expected to *routinely* provide the community with synergistic combinations of techniques that have typically been only accomplished to date on a one-time or heroic basis at other facilities.

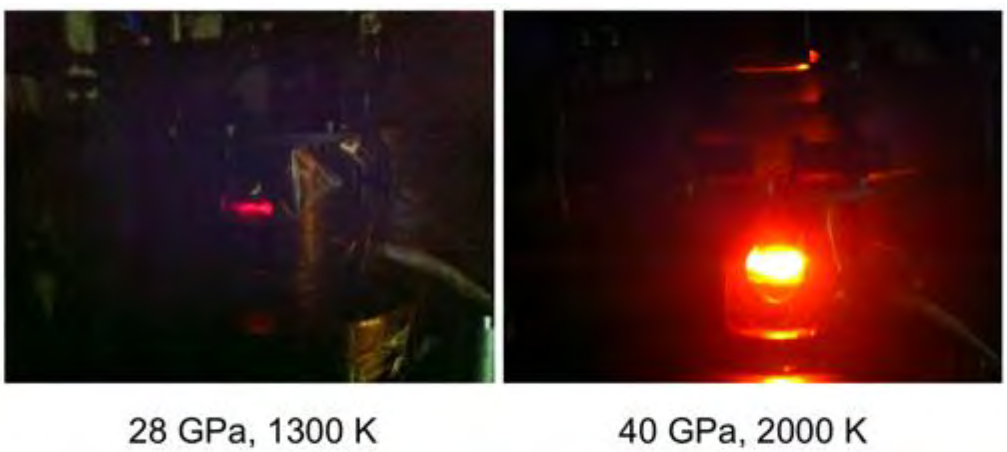

Figure 5. Images of the modified Liermann cell at the ALS in radial diffraction mode during an externally-heated high pressure, high temperature experiment. Temperatures were calibrated using Pt-Rh thermocouples, and pressures from the equation of state of iron. The conditions on the right represents the highest sustained temperature achieved using external heaters within the diamond anvil cell. These experiments are described in more detail in Miyagi et al. (Rev. Sci. Instrum., *84,* 025118, 2013).

COMPRES IV: ALS Plans Moving Forward

We will surely continue to deploy COMPRES staff to assist users with varying levels of expertise with routine needs, such as 300 K axial and radial diffraction measurements: and, we anticipate enhancing the degree of automation, pressure-temperature control, and ability to operate the beamline remotely in the next five years as part of our overall efforts towards making our facility as user-friendly as possible. Beyond these standard expectations, we expect that over the course of COMPRES IV the major signatures of both staff and infrastructure-development focus will be in making novel and challenging multi-technique experiments much more routine for users. For example, a clear agenda of the first two years of COMPRES IV is to make high-pressure single-crystal diffraction experiments routine under external-heating. The scientific motivations for such studies are multi-fold, and include characterizing the precise structures and equations of state of volatile-bearing phases (primarily H- and C-bearing materials) at the pressures and temperatures of relevance to subduction, including as they approach the conditions at which they release their volatiles. Indeed, whether even the structures of the phases that are actually devolatilizing during the subduction process have all been characterized to date is unclear (e.g., Figure 4). Similarly, whether the devolatilization process of materials during subduction is simple and abrupt in P/T space, or proceeds through intermediates (as is often the case at ambient pressures) is unclear. Thus, with a combination of external heating (accessing temperatures of order ~1000 K or more) and single crystal diffraction, we may be in a position in the next few years to answer not only the question of *what* is dehydrating at depth, but may also be able to address *how* materials dehydrate at depth.

By the same token, our coupling of radial diffraction experiments with extreme external heating and a combination of external heating and laser-heating to reduce temperature gradients remain challenging and state-of-the-art measurements (e.g., Figure 5). One of our goals during COMPRES-IV is to refine these techniques and codify best practices so that they become substantially more routine for users: we believe that this is an eminently achievable goal that is strongly motivated by the scientific interest of these measurements. In short, the ability to make strength measurements of candidate mantle materials at the pressure and temperature conditions of the lower mantle is a rich and insufficiently tapped area. For example, the effects of many extrinsic parameters such as grain size, water content, and the interplay between oxygen fugacity and defect chemistry on rheology have been largely unprobed at lower mantle conditions. Thus, we expect that detailed constraints on the rheology of Earth's deep mantle may be in reach, but will require a substantial amount of effort to both facilitate difficult measurements, and to make them accessible to a broad portion of the community.

Lastly, we expect that COMPRES IV will represent a time period in which synergies between 12.2.2 and other beamlines at the ALS will be emphasized. For example, over the course of the development of our single-crystal enterprise, we have extensively interacted and consulted with crystallography beamline 11.3.1 (at which there is experience in doing crystallography at pressures to ~8 GPa). With the extended closure of the infrared enterprise at NSLS, ALS infrared beamline 1.4.4 has (driven by close collaborator of the COMPRES 12.2.2 PI and NSLS-IR PI Zhenxian Liu) been set-up in the last six months for high-pressure infrared experiments (both the sample prep lab and miscellaneous infrastructure of 12.2.2—breadboards, optic mounts, etc.---assisted with this development). We expect that extensive synergies will exist between the diffraction expertise of 12.2.2 and the newly established high-pressure infrared capabilities of 1.4.4 moving forward---in this sense, ALS is fully poised in the first two years of COMPRES-IV to take on the combined X-ray/vibrational synergy previously deployed by COMPRES at NSLS-I. By the same token, the Laue microdiffraction beamline at 12.3.2, which is capable of conducting rapid diffraction across samples at the sub-micron length-scale, has only been deployed occasionally on quenched high-pressure/-temperature samples (e.g., Friedrichs et al., 2010): yet, this technique holds the prospect of detailed, highly spatially resolved characterization of quenched high P/T samples. Thus, during COMPRES IV, we plan to strongly promote interactions with 12.3.2 moving forward, given its capability to resolve differences in phase (and prospectively chemistry) at the sub-micron scale in diamond anvil cell samples.

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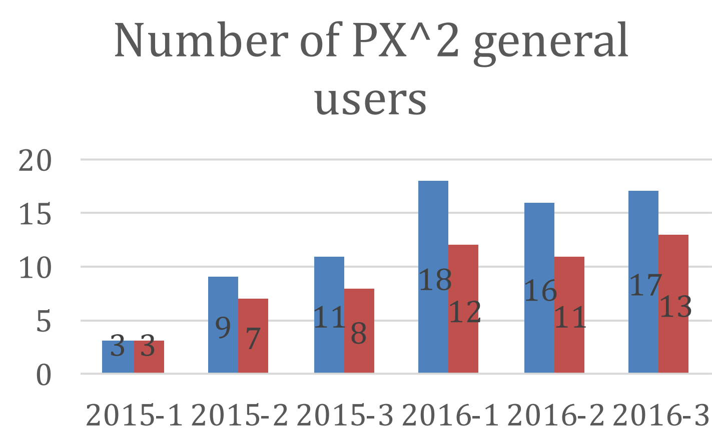
2. APS Beamline 13BM-C PX^2 DAC (PI: Przemek Dera, Univ. Hawaii)

Introduction



Partnership for Extreme Xtallography (PX^2) program is one of the newest COMPRES-supported experimental facilities for high-pressure Earth science research. The PX^2 program is located at the Advanced Photon Source experimental station 13-BM-C at the Argonne National Laboratory, and is operated in collaboration between GSECARS and the University of Hawaii. The primary target user base for this new facility were researchers who conducted Earth science focused research at the NSLS X17-DAC facility, whose access to beam time was significantly limited after the closure of NSLS. PX^2 offers excellent capabilities for conducting powder diffraction and pair distribution function studies in diamond anvil cell, which were in the highest demand at the NSLS X17-DAC facility, and offers novel and unique capabilities for more advanced single crystal experiments. High pressure crystallography is not a new field, but thanks to recent revolutionary improvements in experimental technology and software, in the last decade it has been an area of significant research activities, abundant in exciting discoveries and PX^2 from the very inception has been attracting a lot of COMPRES users. The PX^2 program focuses on X-ray diffraction-based high pressure research with diamond anvil cell. Because of the unique instrumentation available in the new station (6-circle Newport diffractometer) some of the experimental characteristics, including resolution/peak width and angular coverage are dramatically improved, compared to the previous NSLS setup. Besides the focus on powder diffraction and total scattering experiments, PX^2 offers currently unmatched performance for single-crystal experiments in diamond anvil cell, including laser heating of single crystals (currently still in commissioning).

PX^2 program is supported by one full-time COMPRES-funded Beamline Scientist, Dr. Dongzhou Zhang, who is employed by the University of Hawaii, and stationed permanently at Argonne. In the PX^2 partnership GSECARS contributes majority of the engineering and X-ray optics design, as well as help with instrument automation and control, while University of Hawaii provides user support, data analysis software support, training of personnel and users in crystallographic techniques and overall management of the project. The facility also hosts long-term (typically 1-year) visiting intern graduate students. At the moment two such students from the University of Hawaii are conducting research at PX^2. Intern students help with instrument commissioning and develop collaborations with facility users. University of Hawaii also provides discounted cost access to mechanical engineer who manufactures custom components and parts for the needs of the projects.

Instrument Access

The experimental station 13BMC has been used for non-high-pressure surface scattering experiments since 2005, however, the adaptation of the instrument for the needs of the high pressure research required major upgrades and improvements of the X-ray optics and addition of laser spectroscopy system, which were funded by COMPRES in 2014. PX^2 facility opened doors for COMPRES users in February 2015. By the end of July 2016, there have been 74 groups of users that carried out research at the PX^2, with 73% of them coming from COMPRES member institutions. PX^2 instrument has been in high demand, among the COMPRES users, as evidenced by high oversubscription rates. The usage of the 13BMC experimental station is currently split between surface scattering and high pressure research in approximate 2:3 proportion (initial arrangement with GSECARS assumed 1:1 split, however, the

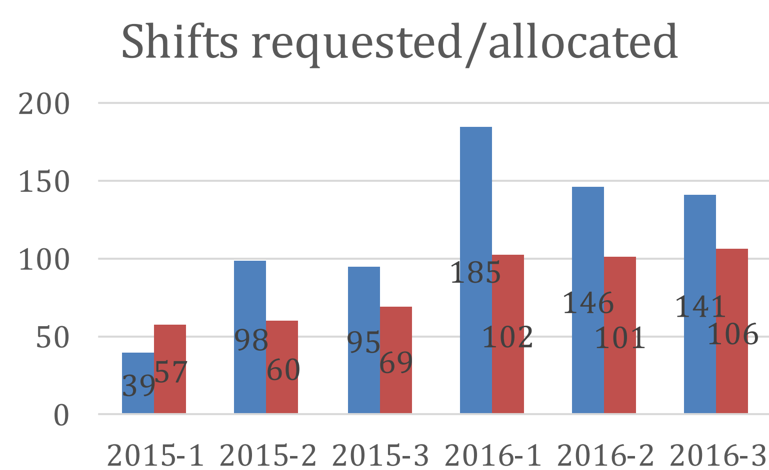


Fig. 2: Statistics of PX2 shifts requested/allocated for each run. Blue bars show the total number of shifts requested by the users, and red bars show the number of shifts allocated to the users. Oversubscription rate (total number of shifts requested/total number of shifts allocated) =1.44.

proportion has been adjusted by GSECARS due to very high volume of mineral physics beam time proposals). During the 2016-3 APS run high pressure program will have available 43, out of 65 total beam time days. All of the instrument time, except for time reserved for commissioning and testing of new components, is distributed based on APS General User Proposals (GUP), which are peer-reviewed by the APS Proposal Review Panel.

Multiple X-ray related techniques, including single crystal and powder diffraction, multi-grain diffraction, pair-distribution function measurement and thermal diffuse scattering, have been utilized by PX^2 users in their studies. Several auxiliary techniques, including resisitive heating setup, membrane pressure controller, ruby fluorescence pressure determination and controlled chemical environments (humidity and oxygen partial pressure), are provided to PX^2 users. Users study a wide variety of samples, including minerals of the Earth's mantle and core, meteorite thin slices, quasi-crystals, organic materials and energy-related materials.

Facility Overview

PX^2 is receives X-ray beam from a bending magnet source, which is characterized by much lower beam flux than insertion devices such as undulators, therefore, from the very beginning of the project our philosophy has been to try to utilize ingenious X-ray optics designs developed by GSECARS scientists, to enhance the amount of X-rays delivered to the experimental hutch and focused onto the sample and make it more than sufficient to study miniscule mineral fragments enclosed in diamond anvil cells. The GSECARS bending magnet branch 13BM receives 6 mrad of horizontal beam fan. A mask close to the shield wall blocks a central 1 mrad section dividing the fan into two separate beams for experimental stations 13BMD and 13BMC. The inboard beam for the 13BMC station is first bounced down by a 1 m long vertical focusing KB mirror, which is located in 13BMB. To maximize spatial separation of the two beams the inboard part of the fan is deflected by a single-bounce Rowland circle monochromator with an exit angle ranging between 10 and 30 degrees. Because of the single-bounce design, the setup operates at fixed energy, since changes of the 13BMC monochromator angle change the beam path in the experimental station. The 13BMC monochromator is designed to hold three different crystals optimized for different energy ranges (8-17keV, 16-20keV, 28-32keV). Until 2014, only 15 keV beam could be used for experiments, which made diamond anvil cell experiments impractical due to excessive absorption by diamond anvils and high scattering angles specific to this energy. With the support from COMPRES and the APS, a second high energy crystal for 28.6 keV X-ray, excellent for high pressure studies, was purchased and installed in 2014. At present the experimental station operates at changeable energies of 15 keV and 28.6 keV. The Rowland circle monochromator utilizes an asymmetrically cut and dynamically bent crystal which focuses the beam in the horizontal direction. Beam focusing in the vertical direction (and removal of higher order harmonic contamination) is achieved with a use of the dynamically bent vertical focusing mirror. Until 2014 the X-ray optics of 13BM-C was capable of producing a beam of approximately 0.250x0.500 mm^2, appropriate for surface scattering, but far too large for diamond anvil cell. The COMPRES funding for PX^2 allowed to commission a new 320-mm long high resolution horizontal second-stage focusing K-B mirror, which was installed in September, 2015. This new horizontal K-B mirror provides a compound focusing capability together with the Rowland circle monochromator. In order to allow very high-pressure experiments (above 50 GPa), this micro-focusing capability of the X-ray is necessary to minimize the background for single crystal diffraction and diffuse scattering measurements. Currently for high pressure research, the X-ray focus size is ~15×15 μm^2.

Since the inception of PX^2, besides monochromator and K-B focusing mirrors, several other auxiliary components have been installed to improve the quality of the X-rays. A hutch entrance shielding with motorized slits and shielded beam transport pipe extending from the hutch entrance to the diffractometer were constructed in 2015 to minimize parasitic background scattering. The shielded beam transport pipes are connected to the sealed horizontal K-B mirror box. Both the pipes and the mirror box are filled with helium gas, which significantly reduces the Compton scattering background from the air, reduces the attenuation of the X-ray in the air, and avoids the erosion from ozone generated by the X-ray in the air. Additional collimation cleanup slit was installed to optimize beam profile and minimize profile "shoulders". The motion control of the cleanup slit is fully motorized, so it is possible to find the best position of the cleanup slit with a micrometer-resolution. This motorized motion control of the cleanup slit is important to the micro-focusing of the X-ray. In the summer of 2016, we installed a new custom X-ray beamstop with a built-in pin photodiode detector, which was developed in collaboration with HPCAT scientists. This integrated beamstop/diode component enables us to monitor the intensity of the X-ray while collecting data, and provides greatly enhanced capability to synchronize the shutter control with detector exposure and sample rotational motion, essential for high accuracy single crystal measurements.

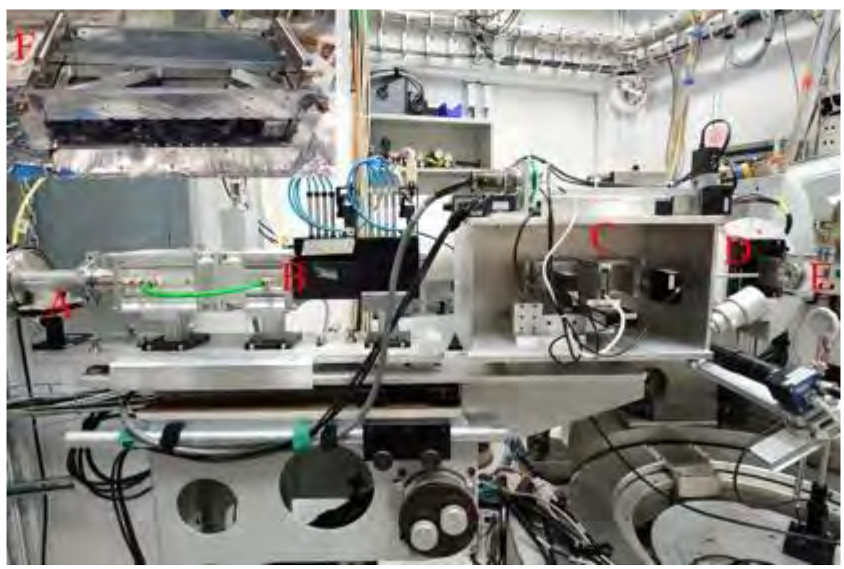


Fig. 3: Major X-ray optics in 13-BM-C for high pressure single crystal diffraction. A: Shielded beam pipe. B: Bench shutter and filter set. C: Horizontal K-B mirror enclosure. D: Motorized cleanup slit. E: Diamond anvil cell. F (inset): Upgraded horizontal K-B mirror.

The experimental station 13BMC is equipped with a unique heavy duty high-precision Newport 6-circle kappa-geometry diffractometer (4 circles for sample rotation + 2 circles for detector rotation). The Newport diffractometer can be used with a wide range of X-ray detectors, including Pilatus 100K and MAR165 CCD, and is compatible with all currently used types of diamond anvil cells. The Newport diffractometer with its high speed (up to 15 deg/sec) high load capacity (up to 25 lb), high precision of rotation (sphere of confusion below 10 micrometers) and exceptional number degrees of freedom available for sample and detector manipulation is an ideal setup for the type of advanced crystallography experiments conducted at PX^2, and the only instrument of this type available for mineral physics research in the country.

PX^2 is dedicated to geoscience research. Contemporary research on Earth-related materials requires not only high pressure, but also high temperature, and resistive-heated diamond anvil cell has been broadly used in recent mineralogy experiments. A resistive-heating and temperature reading setup has been developed and installed in the experimental station 13-BM-C.

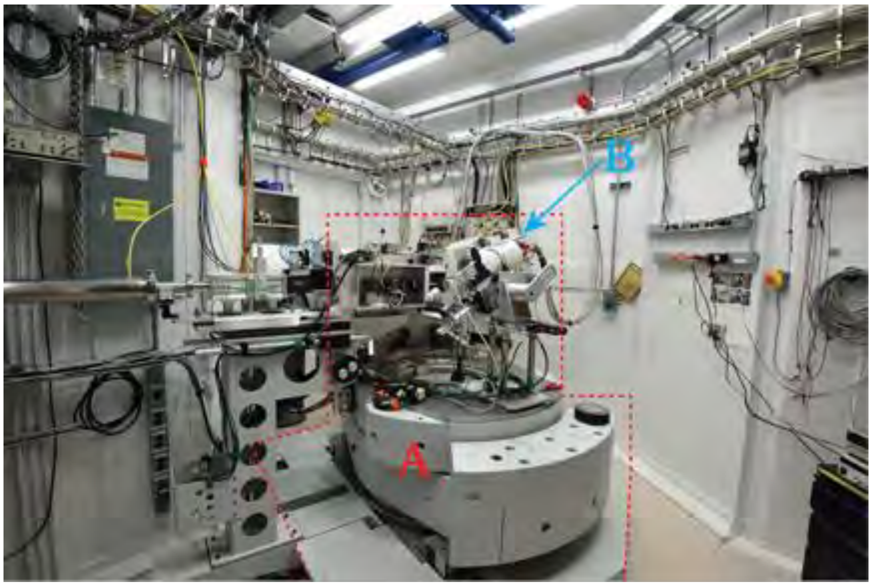


Fig. 4: High pressure single crystal diffraction setup at 13-BM-C with Newport 6-circle kappa-geometry diffractometer (A) and MAR165 CCD area detector (B).

A 1000-W power supply is used to power the heaters in the DACs, and a multichannel digital multimeter is used to read temperatures from thermal couples. Both the power supply and the digital multimeter can be controlled remotely through Ethernet. The setup is capable of heating the samples up to 1500 °C at high pressure. A water-cooling system has been installed to stabilize the sample and the diffractometer. This water-cooling system is compatible with both the membrane pressure controller, and the laser heating system that is under construction. The water-cooling system has been used by more than 10 groups of users to date.

Diamond anvil cells mounted in membrane pressure controller allows pressure to be changed remotely, so as to save time from re-mounting and re-aligning the sample, and is therefore more ergonomic for user operations. A remotely-controlled membrane pressure controller setup has been installed in 13-BM-C. This setup is capable of controlling the compression rate during the experiment. Experimenters can change the pressure of the sample using EPICS remote protocol, without entering into the experimental hutch. A special design of the diamond anvil cell chamber has been developed for the single crystal diffraction experiment in 13-BM-C. This chamber features a large opening angle on both side of the diamond anvil cell, so as to allow as much diffraction signal as possible, which is important for structure solution.

Once fully upgraded, 13BMC will become an instrument truly unique on the international scale for very high-pressure crystallographic studies (currently the only similar diffractometer available is located at beamline I19 at the Diamond Light Source, however, the maximum energy is limited to 28 keV, the minimum focused beam size is 0.060 x 0.090 mm, and the instruments primarily serves materials science and chemistry communities). The 6-circle goniometer brings major advantages to the quality and coverage of single crystal X-ray diffraction data, allowing to both dramatically increase redundancy as well as resolution of the data and makes structure determination of nonquenchable unknown high-pressure phases much more reliable.

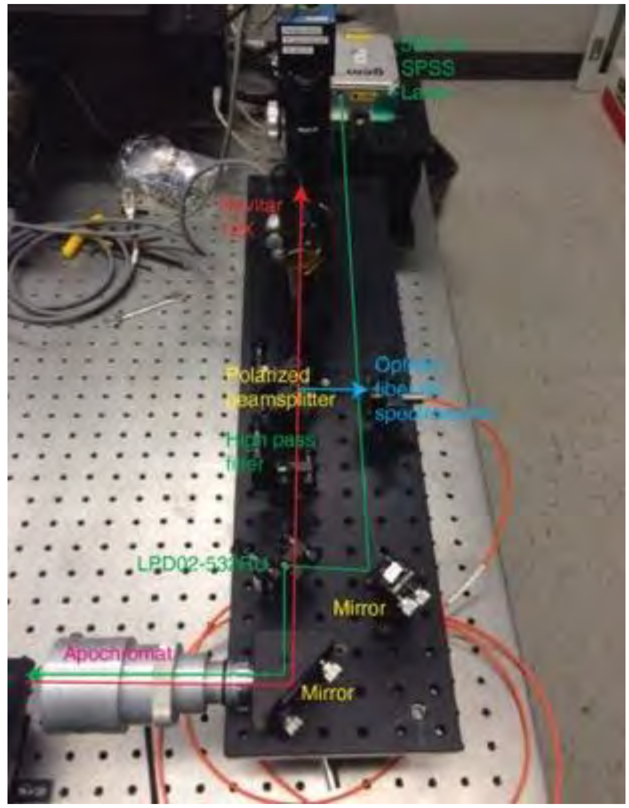


Fig. 6: Retractable sample alignment and online spectroscopy system for PX^2 high pressure single crystal diffraction experiment.

For the convenience and precision of diamond anvil cell alignment, a retractable sample alignment and online spectroscopy system (SASS) with high-magnification zoom microscope was installed in 13-BM-C in 2015. With the Navitar 12X motorized zoom microscope, it allows to quickly and accurately position single crystal samples in the goniometer rotation center. In the spring of 2016, we added a 532 nm solid state laser and an optical fiber coupled spectrograph to the SASS system. Now the compact SASS optical platform is capable of collecting ruby fluorescence signal, so as to determine the pressure of the sample in-situ. We are currently in the process of optimizing the alignment of the SASS, and after this improvement, the SASS optical platform should be capable to collect the Raman spectrum of the sample. A continuous-wave 200 W NIR heating fiber laser (1064 nm) has been purchased and tested. This laser will be incorporated into the SPSS platform, so as to provide laser heating capability for single crystal and powder diffraction. The spectrograph will be used as a temperature reader using blackbody radiation once the NIR fiber laser is commissioned. The psi-axis on which the SAAS optics is mounted is orthogonal to both the omega axis (the typical sample-rotation axis used in single crystal experiments) and to the X-ray beam. The unique mounting of the whole SASS on the psi-platform will allow collection of single crystal data in a psi-rotation mode with a wide angular range allowed by the goniometer, without changing the optical path of the laser light through diamond anvil cell. This approach takes advantage of the ideas introduced by Dubrovinsky et al. in the design of the portable laser heating system used at ESRF, but because of the mounting on a big and very stable psi platform, will offer superior stability and flexibility.

Taking advantage of the two axis detector mount, the 13-BM-C instrument offers capabilities for conducting high-resolution powder diffraction experiments which provide much improved quality of powder data, compared to other, more standard DAC synchrotron setups. By the mounting the area detector far away from the sample on the two circle detector arm, the diffraction signal at any angle stays close to normal incidence with respect to the detector surface, while in case of the traditional DAC setups, the incidence angle quickly becomes oblique, which results in dramatic peak broadening at higher 2-theta angles. Rotation of the detector in both horizontal and vertical planes of the instrument enables covering large 2-theta range, up to 140 deg., is beneficial for both powder diffraction and total scattering.

Scope of research and selected research highlights

Most rock constituents possess well-defined crystal structures and symmetries that control their physical properties. X-ray diffraction experiments reveal details of the atomic arrangement and chemical bonding in these materials, and when carried out at high pressure and high temperature offer insights into atomic-scale response of the crystal to external forces that act on rocks in the Earth interior. New opportunities include routine crystallographic structure determination at pressures beyond 10 GPa, with a number of recent reports successfully resolving crystallographic details of samples at the megabar range. Single-crystal-like analysis of multi-grain data collected on coarse powder samples composed of hundreds of individual crystallites offer new ways to quantitatively characterize development of lattice preferred orientation (LPO) during sample deformation, thus linking crystallographic studies to geophysical-scale flow in the Earth.

Many of the phases formed as a result of pressure-induced polymorphic phase transitions are not quenchable, which means that they revert to the common ambient pressure forms upon decompression. The only way to reveal the secrets of these enigmatic high-pressure structures is to conduct in-situ high pressure crystallographic experiments.

PX^2 started accepting users in 2015-1. Typical publication cycle for synchrotron experiments is 1-2 years, therefore the papers from the first year of operation are starting to come out at the time of submission of this proposal. To date PX^2 users have published 3 papers, with several more currently in review. Two of these first three papers were published in premiere, high-profile journals (Nature and PNAS).

Synthesis of FeO_2 and the Fe-O-H system in the deep Earth

Reference: Q. Hu, et al. FeO_2 and FeOOH under deep lower-mantle conditions and Earth's oxygen–hydrogen cycles. Nature, 531, 241-244 (2016).

The Earth's geochemistry can be regarded as a ternary system of oxygen, its most abundant element by atomic fraction, iron, its major redox ingredient, and hydrogen, its most mobile element responsible for electron transfer. The oxygen rich atmosphere and iron rich earth core represent the two end members of the O-Fe system, overlapping the entire pressure-temperature (P-T) range of the planet. We explored the chemical reaction in the system of Fe-O-H at high-pressure and high-temperature that mimics deep lower mantle (DLM) conditions. When haematite is compressed in O_2 and heated above 76 GPa and 1800 K, a new FeO_2 phase is identified through X-ray diffraction conducted at synchrotron beamlines, including the Partnership for Extreme Crystallography at Advanced Photon Source, Argonne National Laboratory. The spotty FeO_2 diffraction pattern was solved by the so-called multigrain crystallographic method. The newly

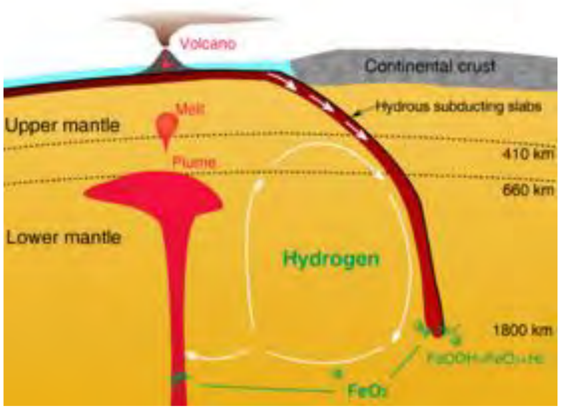


Fig. 7: Hydrogen and oxygen cycles in the lower mantle.

discovered FeO_2 phase holds an excessive amount of oxygen and has the same atomic structure as FeS2. We went on to show that the mineral goethite (FeOOH) can also decompose to FeO_2 at 92 GPa and 2050 K by releasing hydrogen. In DLM situation, the hydrogen released from FeOOH would diffuse, infiltrate or react to form hydrocarbon or other volatiles. At the same time, FeO_2 patches are left in DLM and cumulate through plate tectonics. Such process provides an alternative interpretation to the origin of seismic and many geochemical signatures in the DLM.

Compressional behavior of omphacite to 47 GPa
Reference: Zhang D., Hu Y., and Dera P. (2016) "Compressional behavior of omphacite to 47 GPa" Phys. Chem. Minerals. DOI: 10.1007/s00269-016-0827-4

Omphacite is an important mineral component of eclogite. Single crystal synchrotron X-ray diffraction data on natural (Ca,Na)(Mg,Fe,Al)Si_2O_6 omphacite have been collected at the Advanced Photon Source beamlines 13-BM-C and 13-ID-D up to 47 GPa at ambient temperature. Unit cell parameter and crystal structure refinements were carried out to constrain the isothermal equation of state and compression mechanism. The 3rd order Birch-Murnaghan equation of state (BM3) fit of all data gives V_0=423.9(3) Å^3, K_{T0}=116(2) GPa and K_{T0}'=4.3(2). These elastic parameters are consistent with the general trend of the diopside-jadeite join. The eight-coordinated polyhedra (M2 and M21) are the most compressible, and contribute to majority of the unit cell compression, while the SiO_4 tetrahedra (Si1 and Si2) behave as rigid structural units and are the most incompressible. Axial compressibilities are determined by fitting linearized BM3 equation of state to pressure dependences of unit cell parameters. Throughout the investigated pressure range, the **b**-axis is more compressible than the **c**-axis. The axial compressibility of the **a**-axis is the largest among the three axes at 0 GPa, yet it quickly drops to the smallest at pressures above 5 GPa, which is explained by the rotation of the stiffest major compression axis toward the **a**-axis with the increase of pressure.

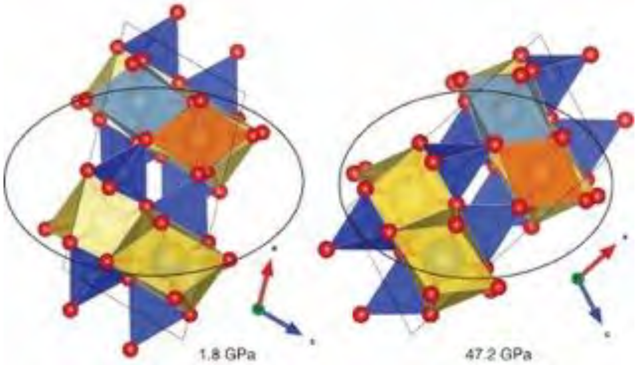


Fig. 8: The orientations of the representation quadric in the **a-c** plane for the isothermal compressibility tensor of omphacite at 1.8 GPa and 47.2 GPa, viewed down **b**-axis.

Future Development Plans

PX^2 program started only 2.5 years ago, and while the instrument is already operational and productive, and in very high demand among COMPRES users, we are still in the process of finalizing the commissioning of laser spectroscopy system. This work is expected to be completed by the end of calendar year 2017. The budget submitted with this proposal does not include any major instrument items, only the regular operation costs.

High pressure in situ single-crystal X-ray diffraction with simultaneous laser heating

High-pressure powder diffraction combined with laser heating (LHPD) is one of the main and most successful experimental methods in mineral physics and high-pressure materials science. The simultaneous high pressure and temperature conditions induce the many dramatic high-pressure transformations which require thermal activation, such as graphite to diamond conversion. Thermal equations of state of the important deep earth minerals can be followed along the geotherm, the temperature distribution with depth in the Earth, to lower mantle and core-mantle boundary conditions, providing information about changes in density that can be correlated with macroscopic observations of seismic-wave velocities at depth. The LHPD technique, however, has a number of intrinsic limitations as well. At high temperature, there is often a significant recrystallization of the sample, which affects the particle statistics. Heated grains, driven by convection, can move away from the heated spot. In addition, the heat transport within the sample is usually not very uniform, and limited by grain-to-grain contacts.

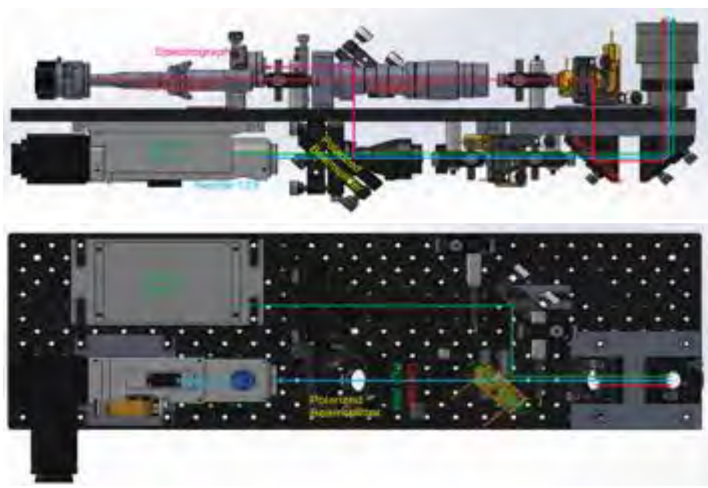


Fig. 9: Design of compact optical table for LHSD experiments. Top panel: side view. Bottom panel: top view. Red, cyan and green lines indicate the IR laser heating, sample observation and Raman spectroscopy optical paths.

Inhomogeneities of the temperature field often cause coexistence of high and low temperature phases and make it difficult to properly characterize crystal structures and phase boundaries. LHPD experiments are not performed in bending magnet experimental stations because of insufficient beam intensity. However, single crystal laser heating (LHSD) experiments, very well suited for a BM station, offer a very attractive alternative to LHPD. In LHSD the temperature distribution within the heated singe grain is much more uniform and predictable, there is no loss of particle statistics due to grain recrystallization, and the quality of the crystallographic information is far superior to LHPD. The challenge of the LHSD experiment with a monochromatic beam is the necessity of rotating the sample during the exposure, which, with the standard stationary laser optics, would require changing the path of the laser beam through the DAC. A new approach to LHSD is with laser and scattered light collected by means of optics attached to the sample rotation stage. The technique was developed at ESRF and produced very high quality single crystal data at temperatures as high as 2500K. We are working on implementation of this approach into the PX2 beamline design. The PX^2 design for laser heating, takes advantage of the unique features of the 6-circle goniometer, with optical platform placed on the very precise heavy duty psi-circle platform.

Single crystal diffraction in natural inclusion-host system

Natural crystals, such as diamonds, when delivered to the surface with ascending magma, often contain inclusions derived from significant depths, and have different paragenetic histories of their origins. The host crystals are usually chemically inert and physically strong, thus providing a nearly perfect container to preserve mineral inclusions from alteration or re-equilibration. Significant efforts have been devoted to characterization of the major and trace element chemistry of the inclusion minerals. One of the important lessons learned from previous inclusion-host studies is that the relationships between the histories and properties of inclusions, host crystals and the rocks, in which the hosts are embedded, are complex. The inclusion and the host crystals can crystallize either at the same time, or one after another. Understanding the formation scenario is critical for drawing conclusions about the paragenetic environment and conditions, particularly in the case of multiple inclusions in the same host. While we have a reasonable understanding of the mineralogy and major element chemical composition of the mantle, the oxygen fugacity is not nearly as well understood, particularly where redox reactions involving carbon are concerned. Natural inclusions in diamond provide good scenarios to examine the redox conditions of the mantle when the inclusions were crystalized. Good characterizations of the inclusions are needed in order to study the redox conditions at the time of crystallization. Previous analytical probes used to study inclusions that address the details of chemical composition and trace elements were usually *ex situ* methods. These require the inclusion to be either exposed or completely liberated from the host. The advantage of these methods is that more accurate information can be obtained via direct access to the sample; however, this is at the expense of the inclusion losing its original residual stress environment and jeopardizes the chemically insulating encapsulation. *In situ* methods, which probe the inclusion through the diamond, have to deal with more complex corrections and calibrations, but in return offer a fully non-destructive approach that can still provide very valuable information. Synchrotron micro-focus X-ray diffraction, which can be applied *in situ*, offer very good alternatives to exclusively *ex situ* experiments such as electron microprobe analysis (EPMA), but require some further developmental efforts to reach the required reliability and accuracy levels, e.g. accounting for the absorption and extinction effects caused by the host. At PX^2, we propose to develop a set of improved, reliable methods for nondestructive *in situ* analysis of natural inclusions, allowing determination of crystal structure, major element chemistry, cation ordering and oxidation state. We will incorporate the existing single crystal diffraction capability at PX^2 with the X-ray Absorption Near Edge Spectroscopy (XANES) and micro-tomography capabilities at GSECARS to study our samples. We plan to apply this methodology to study a suite of solid inclusions in preselected natural samples and derive reliable information about the composition, mineralogy, oxygen fugacity and water content of the mantle rocks.

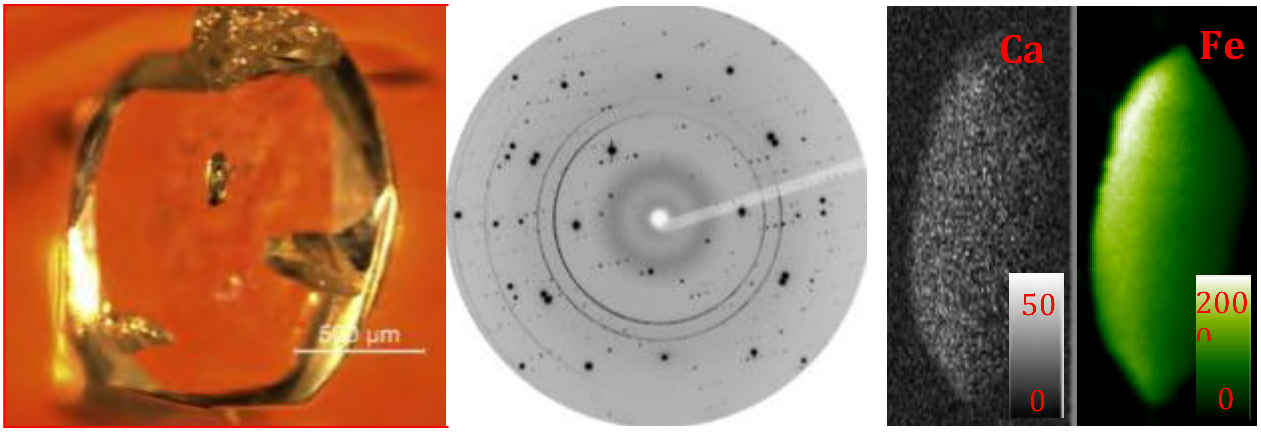


Fig. 10: Left: Optical image of one Udachnaya diamonds with orthoenstatite (oEn) inclusion investigated during our preliminary experiments at PX2. Middle: Single crystal diffraction pattern of the oEn inclusion. Right: Ca and Fe concentration map of the oEn inclusion from preliminary *in situ* XANES study.

3. APS Gas Loading for DAC (PI: Mark Rivers, Univ. Chicago)

Overview

The COMPES/GSECARS gas loading system at the APS has been a major advance for the U.S. diamond anvil cell community. Prior to the installation of this system in 2008 the use of noble-gas pressure media was restricted to a small number of scientists with access to systems at the Carnegie Institution or the Lawrence Livermore Laboratory. The COMPRES/GSECARS system has led to the improved hydrostatic conditions with Ne or He now being the norm for most synchrotron experiments in this country. This has greatly improved the quality of the measurements being made, and the system is available to the entire community.

The system began operation in February 2008 and has been running with minimal downtime since then. The system works extremely well, with the only significant problems being some failures of the commercial compressor. We have in-house technical support (Guy Macha) to repair such problems, and the mean time to repair has typically been 1 day. We have recently purchased a spare compressor, so that we can rapidly swap it if there is a major problem.

One problem that has arisen recently has been a dramatic increase in the cost of neon in the US. The price has increased from about $3,000 for a 6,000 liter cylinder to over $22,000. The gas loading system typically has used 3 cylinders per year. We have solved this problem in two ways. First, we found a supplier of neon in the Ukraine who sells 7,500 liter cylinders for $3,050, or 9 times less than the US price per liter. We have recently purchased two cylinders from Ukraine. Even with an additional $2,000 in shipping costs the cost was about 5.5 times less than the US price. Second, we have been using more neon than necessary because we cannot pump all of the neon out of the large gas cylinder, or out of the pressure vessel when loading is complete. We have recently received funds from COMPRES to purchase a low-pressure compressor. This was installed in May 2016, and has allowed us to solve these problems, greatly reduce our neon consumption.

The COMPRES/GSECARS system at the APS is available for use by any member of the COMPRES community, regardless of whether they are performing experiments at GSECARS, at another APS sector, at another synchrotron, or in their home laboratory. The support from COMPRES allows the system to be available for users who cannot afford the time or money to travel to APS, by providing a “mail-in” service. It also allows the system to be available to users who are conducting experiments at APS sectors other than GSECARS. These include users from sectors 3 (inelastic), 4 (magnetism), 16 (HP-CAT), and 32 (imaging), 34 (microdiffraction), and others.

Personnel

This COMPRES proposal seeks funding for 50% of a staff scientist for the gas loading system. The responsibilities of the COMPRES supported portion of this position are 1) loading cells from the “mail-in” program, i.e. that are sent to the APS by users who do not travel here 2) training and assisting on-site users working at beamlines other than GSECARS with loading their cells. Dr. Sergey Tkachev began in this position in 2010. The other 50% of Sergey’s salary and responsibilities are covered by GSECARS.

Guy Macha is a GSECARS funded technician who provides mechanical support for the system. We do not seek any support for Guy in this proposal.

Figure 1. Dr. Sergey Tkachev with the COMPRES/GSECARS gas loading system

Operations, Performance Metrics

The following table shows the statistics on the usage of the gas loading system since 2010.

Year	Users per year	Unique users per year	Loadings per year
2010	149	55	206
2011	288	86	420
2012	361	109	516
2013	403	145	646
2014	360	156	562
2015	531	163	738
2016 (to 6/19)	246	77	323
Total	**2338**	**784**	**3411**

As an example of the past performance on this project, the following table summarizes the mail-in service for the year from November 2014 through October 2015.

University	Name	Number of DACs loaded
University of Illinois at Urbana-Champaign	Huihui Pan + Vlad Iordache	4
University of Nevada Las Vegas	Kelly Seaborg	1
Stanford University	Zhao Zhao	4
Yale University	Kanani Lee + Kiersten Dawau + Neala Creasy	7
Arizona State University	Dan Shim	7
University of Western Ontario	Yang Song + Mauritz van Zyl	4
Northwestern University	Josh Townsend + Jane Berkowitz	2
Princeton University	Camelia Stan	1
Los Alamos National Laboratory	Matt Jacobsen	8
Oakland University	Yuejian Wang	2
University of Chicago	Yejun Wang + Yishu Wang	8
TOTAL		**48**

In addition to this mail-in service, there were 640 diamond anvil cells loaded in this year. 199 of these cells were prepared for experiments at GSECARS, while the remaining 441 were prepared for experiments at other APS sectors, home laboratories and other synchrotrons. The gas loading of all 640 cells were directly assisted by Sergey. Thus on average he is assisting in gas loading of more than 2 cells every working day. The number of cells loaded per year has been approximately constant for the past 3 years, after growing rapidly in the years 2009-2012.

Sergey spends more than 60% of his time assisting such users and providing the mail-in service. Because of the constantly growing usage of the GSECARS/COMPRES gas loading system during the normal APS user operation periods, significant time is required for repairs and preventative maintenance for the valves and commercially built compressor. Sergey and Guy perform these tasks, during the downtime between the APS beamtime cycles.

Publications
Users of the gas loading system have reported 137 publications during the period 2011-2016. There have certainly been more than this, because not all users have reported that their publication used the gas loading system. At least 50% of the ~700 diamond cell publications from GSECARS and HP-CAT in this period have used the gas loading system.

Community/Broader Impacts
The success of the COMPRES/GSECARS system design has led other groups to copy many aspects of it for systems of their own, including HPSync at the APS. In addition four other identical units have been built by the University of Chicago Engineering Center. These have been sold to Jennifer Jackson at Caltech, the Advanced Light Source at the Lawrence Berkeley National Laboratory (where it is available to users of the COMPRES supported high-pressure beamline, 12.2.2), Sandia National Laboratory, and the LNLS synchrotron in Brazil. Sergey has provided valuable expertise and hands-on support during construction for these new gas loading systems. There are expressions of interest for additional systems, both in the US and abroad.

Planned Activities
We propose to continue all activities listed in the previous sections during the next COMPRES funding cycle (June 2017 – May 2022).

4. APS Sector 3 Inelastic X-ray Scattering, Nuclear Resonant Scattering, and Mössbauer Spectroscopy under extreme P-T conditions (PI: Jay Bass, UIUC)

High-resolution inelastic X-ray scattering (IXS) techniques provide the Earth and Planetary science community with unique opportunities for measuring the properties of materials under extreme pressure and temperature (P-T) conditions. Experiments at P-T conditions to 300 GPa and between 3000-4000 Kelvin are presently possible. Our proposed Facility project is aimed at enabling the COMPRES community to exploit these new and powerful capabilities, conduct education and outreach, support and expand the user base for various IXS techniques, and create state-of-the -art characterization tools. Scientifically, we will enable measurements of the electronic, thermodynamic, thermoelastic, and chemical properties of materials under the high P-T conditions of planetary interiors relevant to geophysics, petrology, and the geochemistry of rocks, minerals, and of meteorites.

We provide three different advanced X-ray spectroscopy techniques, namely, Synchrotron

Mössbauer Spectroscopy (**SMS**), Nuclear Resonant Inelastic X-ray Scattering (**NRIXS**), momentum-resolved inelastic X-ray scattering (**IXS),** plus offline conventional Mössbauer spectroscopy (**CMS).** The unique electron-bunch time structure and high X-ray flux above 10 keV makes the APS the only practical source for inelastic X-ray scattering in the USA. COMPRES users will have access to i) on-line SMS during the 24-bunch and hybrid-filling modes, ii) on-line NRIXS during the 24-bunch mode, iii) on-line IXS studies with access to the high energy resolution HERIX-3 and HERIX-30 instruments, based on GUP or PUP proposals, and iv) off-line Mössbauer spectroscopy, available by mail-in or drop-in service.

SMS and NRIXS: SMS is a unique and an effective technique to determine the valence, spin state, magnetic ordering, coordination number, ligand orientation, local distortion, and spin - valence fluctuation rates of Fe in iron-bearing minerals. Other than Fe, we also have high-pressure capability for materials containing Kr, Sn, Eu and Dy. NRIXS is used to determine the phonon density of states, a very rich source of information that constrains electronic, thermodynamic and elastic properties, sound velocities, force constants, vibrational entropy, and Gruneisen parameter (Chen *et al.*, 2012; Gu *et al.,* 2012). As such, NRIXS has been in high demand among the geophysics community, for example to determine the sound wave velocities of Fe-C (Gao *et al.*, 2009; Chen *et al*, 2012; Chen *et al.* 2014), Fe-Si (Lin *et al.,* 2003; Mao *et al.*, 2012; Liu *et al.*, 2014; Liu *et al.* 2016) and Fe-Ni (Liu *et al.*, 2016), and Fe-H (Mao *et. al.*, 2004), and Fe-S (Lin *et al.*, 2004) systems. Geochemists recently recognized the potential of isotope fractionation as a proxy for oxygen fugacity to determine redox conditions during silicate melt segregation related to the evolution of the core-mantle boundary, lower mantle and crust (Polyakov 2009). These studies require different data collection and analysis strategies. Much of the pioneering work was done in the 2012-2015 period (Dauphas *et al.*, 2012; Hu *et al.*, 2013; Dauphas *et al.*, 2013; Blanchard *et al.*, 2015; Roskosz *et al.*, 2015).

IXS: Momentum-resolved inelastic X-ray scattering techniques measure phonon dispersion relations from single crystals, powders, glasses and liquids. One major accomplishment during the 2012-2016 period was the development of capabilities for single-crystals in DAC's, and on-line crystal XRD orientation using a fast-readout area detector purchased with COMPRES infrastructure funds. IXS is now a mature technique for geophysical research as a result of advances in X-ray focusing optics and development of two advanced spectrometers at the APS: HERIX-3 (at Sector 3) and HERIX-30 (at Sector 30).

Experiment using the above three techniques are performed at the 3-ID and 30-ID beamlines based on general user proposals (GUP's). During the period 2012-2016 August, there were 126 and 67 GUP requests from Earth science and high-pressure research groups for 3-ID and 30-ID, respectively. A breakdown of beamtime request is each year is shown in Table 1 of Appendix A. A full list of beamline users from is listed. Of these GUP requests 89 (71 % of the total requests) and 36 (54%) were granted beam time at Sector 3-ID and 30-ID, respectively. These percentages are well above the average acceptance rate, which is below 30%. The relatively high success rates for COMPRES proposals are due to the excellent quality of research that these techniques attract from the COMPRES community, and partly due to the COMPRES-funded scientist, Dr. Wenli Bi, working with COMPRES PIs to develop effective proposals that are highly competitive for beam time.

Conventional Mössbauer Spectroscopy (CMS): Similar to SMS, CMS provides information on the valence, spin state, magnetic ordering temperature, coordination number, local distortion, and spin and valence fluctuation rates of iron and more than a dozen other elements. The Mössbauer Laboratory at the APS was made available to COMPRES researchers 5 years ago as a service and research tool. Initially, users were General Users who needed additional characterization of samples before or after experiments at the beamline. With the purchase of a "point source" (400 µm in diameter), taking spectra from samples inside the diamond anvil cell or recovered samples from high-pressure experiments has become routine (e.g., Fig. 1, Appendix). Since 2011 there has been growing interest from the COMPRES community in this lab-based facility. We offer free mail-in or drop-in service throughout the year. User can send samples and we prepare them, collect, analyze and interpret the data, and communicate the results back to users. We also write sections of manuscripts on the Mössbauer results. Often the samples are loaded in diamond cells or are recovered from previous high-pressure experiments, in which case careful alignment of the sample with respect to the point source is critical.

Since 2011, 266 samples from 22 geoscience and high-pressure research groups have been measured in the Mössbauer Laboratory. The-breakdown of samples measured in the lab in each year from 2011 to March of 2016 and a full list of users from geoscience community are shown in Figure 2 and Table 3, respectively, in Appendix A.

Science highlights from 2012-2016

High-Spin Low-Spin Transitions in Glasses and Melts: Properties of rock-forming silicate melts at *P-T* conditions of the mantle are crucial for understanding the fractionation of Earth's mantle during its early evolution. The state of Fe in Al-bearing silicate glasses at high pressure was found to remain in the high-spin state, rather than undergoing a spin-pairing transition as proposed previously. Using the silicate glass results as an analog for understanding silicate melts, the results indicate that iron likely experiences significant changes in local environments yet remains overall in the high-spin state in silicate melts at the extreme *P-T* conditions of the deep mantle (Mao *et. al.*, 2014).

Velocity-Density Relations of Fe-Alloys: IXS experiments on Fe-Si led to new compressional wave velocity-density ($V_P-\rho$) models of Fe alloys as a means of determining the chemical composition of the core. $V_P-\rho$ relations of Fe alloys at relevant *P-T* conditions is critical for evaluating the composition and seismic signatures of the core. Comparisons between the $V_P-\rho$ profiles of the core and candidate Fe alloys provide first-order constraints on the amount and type of potential light elements—including H, C, O, Si, and/or S— that are needed to compensate the density deficit of the core (Mao *et al.*, 2012).

Fe Isotopic Fractionation: The equilibrium Fe isotopic fractionation factors of minerals like goethite and jarosite are important for interpreting Fe isotopic variations in low-temperature aqueous systems on Earth and possibly on Mars in the context of future sample return missions. Biogeochemical transformations of Fe-bearing minerals and their relationships to dissolved species can be investigated by measuring Fe isotope variations in rocks, minerals and fluids However, a major impediment to applying this method is that most equilibrium fractionation factors (β-factors) have not been rigorously determined. NRIXS yields force constants, which can be transformed to β-factors (Polyakov *et. Al.*, 2007). Iron isotopic fractionation can now be succesfully measured at high-pressure or high-temperature conditions for Earth science research.

Tin Isotopic Fractionation: At Sector 30, tin isotope fractionation studies recently became feasible with the availability of a high-throughput cryogenically-cooled high-resolution monochromator (Toellner *et al.*, 2011) and optimized undulator with short period. Siderophile elements provide clues to the conditions under which terrestrial planets differentiated into metallic cores and silicate mantles. Studies of Sn isotopic fractionation will allow the thermodynamic conditions prior to differentiation (P, T, fO_2) to be constrained.

Fe melting and Laser Heating Advances: SMS studies at Sector 3 are addressing fundamental questions such as the temperature at the center of the Earth. New methods were developed to better determine the melting point of iron (Jackson *et al.*, 2012; Zhang *et al.*, 2015). It was found that iron melts at higher temperatures than previously reported with other techniques (Jackson *et al.,* 2013).

Carbon in the Core? NRIXS based research on Fe_7C_3 shows that it may have the right seismic wave velocities at high pressure to match those of the inner core. Studies at Sector 3 provided the first estimates of seismic wave speeds in this Fe-carbide at core conditions and suggest that its velocity behavior is due to a change in the electron spin configuration of Fe. The results suggest that the Earth's core is rich in Fe_7C_3, and may explain where some of Earth's "missing carbon" is hiding (Chen *et al.,* 2014).

Scientific and Technical Accomplishments in 2012-2016 period

1. The Mössbauer Spectroscopy laboratory was made compatible for high-pressure experiments by purchasing a ^{57}Co point source and building a motorized 3-axis stage with micron resolution. A new enclosure (mini-hutch) was built for safe and quick sample change. Over 266 samples have been measured and characterized.
2. Implementing an area X-ray detector for the HERIX-3 IXS spectrometer in 3-ID-C, enabling single-crystal orientation in the DAC, and determination of the full elasticity tensor.
3. Implementation of external heating of DAC's for the HERIX-3 spectrometer for high *P-T* studies [5, 16].
4. Development of IXS for powder samples in a DAC at HERIX-3 (Liu *et. al.,* 2014). With funds provided by APS a new KB mirror system was installed in tandem with a toroidal system, focusing the beam to ~17 microns with good efficiency (Alatas *et. al.*, 2011).
5. Development of the FASTER system for rapid temperature readout in laser heated DAC measurements in the 3-ID-B NRIXS station (Zhang *et. al.*, 2015).
6. Implementation of an on-line ruby pressure measurement system in 3-ID-B.
7. Development of a gas membrane-driven panoramic DAC for NRIXS studies.
8. Development of a cryostat and a miniaturized gas membrane-driven DAC for low temperature high-pressure NRXIS and SMS experiments, the first and only instrument of its kind in the world (Bi *et al.*, 2015; Bi *et al.*, in prep).
9. Development of new high-pressure compatible instrumentation at 30-ID-C for sound speed measurements using the HERIX-30 IXS spectrometer.
10. Development of Sn Mössbauer isotope studies at Sector 30. This is the strongest nuclear resonant source for Sn worldwide by a factor of ten.
11. Exploitation of the APS hybrid mode to achieve SMS data with improved accuracy.
12. Workshops in 2012 and 2014 (40 participants attending each workshop) for nuclear resonant scattering data analysis using CONUSS, PHOENIX, and SciPhon. Due to high demand, a workshop will be held in Nov. 2016.

13. An offline Raman system that was previously located at GSECARS and recently moved to sector 3. The system has been reconfigured for laser safety control and activated for use for general users. This system will allow users to measure pressure from the diamond Raman edge at extreme pressures (~1Mbar and above) where ruby fluorescence spectra are difficult or impossible to observe. Users will also be able to measure Raman spectra from samples under pressure. The latter provides complimentary information to the NRIXS and IXS data about pressure-induced phase transitions. Dr. Wenli Bi will maintain the system and assist users.

Over the last 5 years we initiated high-pressure experiments at the new IXS beam line (sector 30-ID) and made numerous improvements to experimental capabilities of the NRS and IXS beam line (sector 3-ID) to enhance performance for high-pressure research. We will continue to offer special capabilities for SMS, NRIXS, IXS (HERIX-3) and X-ray diffraction in the 3-ID-B and 3-ID-C stations, combined with laser or external heating. The HERIX-30 spectrometer is added as a new tool available to the COMPRES community. All of these distinct inelastic scattering methods are in many ways ideally and uniquely suited for addressing a variety of important geophysical questions.

Proposed work for 2017-2022 period

During this period, we plan to implement

1. Fast Chopper for SMS studies to boost the data acquisition rate by two orders of magnitude. During the next few years, we will add a new capability for SMS: a fast chopper in station 3-ID-D. This will open unprecedented possibilities for the Earth science community. The fast chopper will be the first of its kind. We expect to decrease the data collection time by two orders of magnitude for SMS in the hybrid mode. This will essentially increase the beamtime available, enable studies of reaction rates in temperature and pressure dependent processes with high precision, and make on-line laser-heated material synthesis and characterization feasible.
2. New X-ray focusing system combining a compound refractive lens and mirror for station 3-ID-D to enable high-pressure experiments using the fast chopper.
3. Acquisition of array APD detectors or stacked detectors for NRIXS and SMS measurements to improve the time resolution and count rate.
4. Implementing efficient polarizer/analyzer optics for studies of magnetism at high pressure.

The above projects will be funded primarily by the APS.

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Appendix

Table 1. The general user proposals for high pressure related activities at 3-ID and 30-ID. (*) Statistics from 2016 is projected based on the beamtime cycle 1 and 2 up to August.

Year	3-ID requested	3-ID allocated	30-ID requested	30-ID allocated
2012	26	21	17	6
2013	29	22	12	8
2014	20	15	13	7
2015	15	11	10	7
2016*	27	15	10	6
Total	117	84	62	34

Table 2. 3-ID and 30-ID beamline users from COMPRES community and other high-pressure and geosciences research groups in 2012-2016 period. Many of the users were allocated beam time repeatedly.

PI	Institutions	PI	Institutions
Thomas Duffy	Princeton Univ.	Shun-ichiro Karato	Yale Univ.
Jennifer Jackson	Caltech	Jung-Fu Lin	Univ. of Texas
Brent Fultz	Caltech	Steven Jacobson	Northwestern Univ.
Dan Shim	Arizona State U	Andrew Campbell	Univ. of Chicago
James Schilling	WashU	Michael Krawczynski	WashU
Viktor Struzhikin	CIW	Bin Chen	Univ. of Hawaii
Nicholas Dauphas	Univ. of Chicago	John Tse	Univ. of *Saskatchewan*
Jay Bass	UIUC	Mathieu Roskosz	Muséum National d'Histoire Naturelle Mineralogy
Barbara Lavina	UNLV	Jackie Li	Univ. of Michigan
Wenli Bi	UIUC/ANL	Wendy Mao	Stanford Univ.
Moshe Pasternak	Tel Aviv Univ.	Michael Hu	ANL

Oliver Tschauner	UNLV	Olivier Delaire	ORNL
John Budai	ORNL	Frank Weber	Karlsruhe Institute of Technology
Ding Yang	CIW	Jason Hancock	Univ. of Connecticut
Iota Valentin	UNLV	Raphael Hermann	ORNL

Table 3. List of users in the Mössbauer lab from geosciences and high pressure physics community.

PI	Institution	PI	Institution
Thomas Duffy	Princeton Univ.	Przemyslaw Dera	Univ. of Hawaii
Bin Chen	Univ. of Hawaii	John Tse	Univ. of *Saskatchewan*
Jay Bass	Univ. of Illinois Urbana-Champaign	Ercan Alp	Argonne National Lab
Dan Shim	Arizona State Univ.	William Basset	Cornell Univ.
Shun-ichiro Karato	Yale Univ.	Barbara Lavina	UNLV
Takamitsu Yamanaka	CIW	Brent Fultz	Caltech
Jennifer Jackson	Caltech	Michael Krawczynski	WashU
Susannah Dorfman	Michigan State Univ.	Nicholas Dauphas	Univ. of Chicago
Jung-Fu Lin	Univ. of Texas at Austin	Mathieu Roskosz	Muséum National d'Histoire Naturelle Mineralogy
Christy Till	Arizona State Univ.	Jackie Li	Univ. of Michigan
Kanani Lee	Yale Univ.	Eran Greenberg	GSECARS

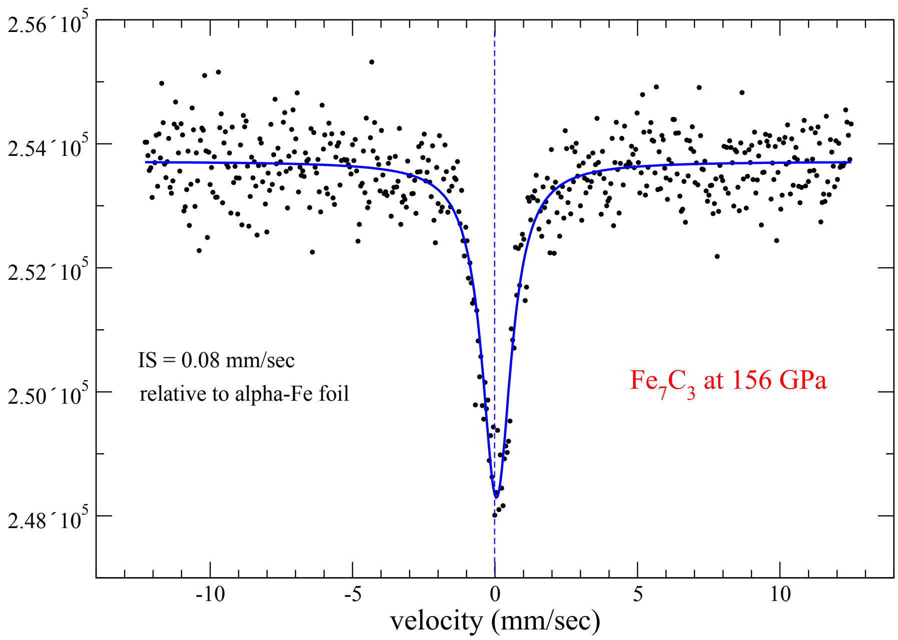

Figure 1. Mössbauer spectrum of Fe_7C_5 at 156 GPa in DAC taken with a point source in the Mössbauer lab. The sample was from Dr. Bin Chen after a NRIXS experiment at 3ID-B. The data collection time is ~ 2 weeks.

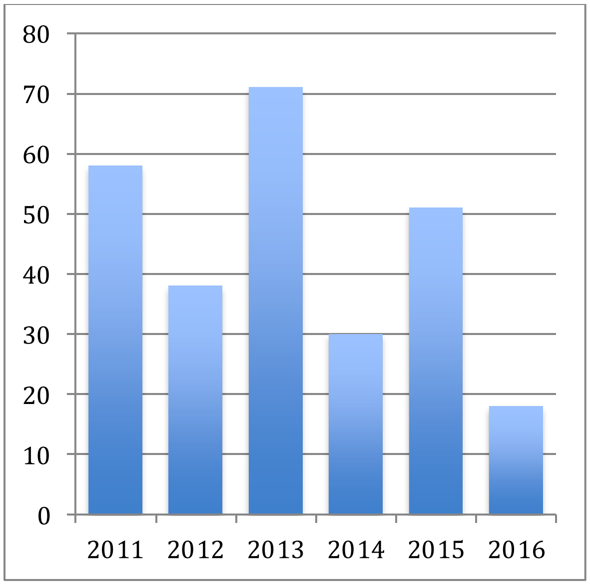

Figure 2. Number of samples measured in the Mössbauer lab from 2011 to August, 2016.

5. Multi-Anvil Development/Cell Assembly Project (PI: Kurt Leinenweber, ASU)

The multi-anvil development/cell assembly project (MADCAP) began from an idea suggested at the very first organizational meeting for a new high pressure Consortium held at Scripps Oceanographic Institute in La Jolla, California - the Consortium later to be called COMPRES. David Walker had the idea that the Consortium needed a "centralized machine shop" for making multi-anvil parts. This idea led to the Multi-Anvil development project that was included in the first COMPRES proposal and the project, located at Arizona State University (ASU), has been a crucial part of COMPRES since the beginning by supporting users around the country and world both in individual research labs and at major synchrotron facilities. The concept of the centralized machine shop developed over time in two directions. Firstly, it is a community-based development project to support multi-anvil users by developing new methods and approaches to high pressure experimentation, and secondly, it is a supply project for cell assemblies for multi-anvil experiments. The machine shop facility at ASU is used to make prototypes and cell assembly parts not amenable to being made outside, while also transferring as much of the work as possible to outside shops in order to save money and to free up the ASU shop for new developments. The developed cell assemblies are curated and carefully characterized at ASU as well as at other participating laboratories, who then use them for their experimental work. A sample of papers resulting from the project and from the use of the cell assemblies is given in the References section.

The project has been called the Multi-Anvil Cell Assembly Development Project up until now, but in the new phase of COMPRES the name is being updated to MADCAP to emphasize the fact that the project aids in the development of multi-anvil (MA) technology itself, as well as the cell assemblies and materials.

Results from the Current Cycle of COMPRES (2012-2017)

Membership
Members of the community who have been involved in the COMPRES Cell Assembly Development Program from 2012 to the present are listed in Table 1. These laboratories participated in the development of new assemblies and improvements to the existing assemblies, were users of cell assemblies, or both.

We have found that this project allows better communication between laboratories than existed before the project began. The findings of the project, in terms of cell designs and multi-anvil technological information, are open to the public and have been published (Leinenweber et al., 2012; Leinenweber et al., 2006; Stoyanov et al., 2010; Hernlund et al., 2005). The discussions that take place among the various laboratories involved in the project become part of the information that is openly shared in the community, including vendors and sources of materials, methods of fabricating assembly parts, and all the details on how to use the materials to have successful experiments. This has enabled many new young investigators to set up laboratories much more easily and quickly than if they had to pursue all the developments on their own.

Development program
The development program, funded by COMPRES, was used to design and create new cell assemblies to serve demands from the community and to maintain or improve the designs of the existing cell assemblies, over the period of 2012-2017. Table 2 shows the complete list of standardized COMPRES assemblies.

DIA assemblies
The choice of where to focus development efforts is based partly on the most important missing or evolving capabilities, and partly on community demand. One major development in the current COMPRES cycle was the greatly increased involvement in DIA assemblies. When the machine shop at Stony Brook closed in 2012, there was an urgent need for an alternative source for the Stony Brook DIA assemblies that had been made in the Stony Brook machine shop for more than 20 years. Matthew Whitaker and Kurt Leinenweber worked together to compile all the information on dimensions and designs that had been developed over the years at Stony Brook. The result is that there are currently three basic DIA assemblies in the program: the S-DIA (standard high pressure cell), the D-DIA (deformation cell) and the U-DIA (ultrasonic cell). The DIA assemblies were previously made entirely at the Stony Brook shop, but we were able to arrange forseveral of the parts to be made commercially in large batches. The graphite furnaces and the boron nitride capsules are the major parts that still must be made in-house because the furnaces are thin and fragile and boron nitride is air sensitive requiring special handling. The three DIA assemblies have been provided to the beam lines (NSLS and now APS Sector 6) since 2012. New types of piston, buffer rod, and pressure medium have been made on a prototype basis since then.

A DIA project at the ESRF, involving Paul Raterron and Nadege Hilairet, was also picked up by the project. The designs supplied by the ESRF project were made in prototype batches and tested at ESRF, then redesigned until a stable configuration was reached. These are now made for the ESRF project on demand on a cost basis.

More recently, GSECARS has transferred their seven DIA designs to us and in 2016 we made test batches of four of the designs in the ASU machine shop as part of the development project. These prototypes are being tested in the current beam cycle. When the designs are stabilized, the plan is to produce a portion of the parts outside of ASU, except again for the parts that cannot be made reasonably outside of our shop (fragile parts, boron nitride parts, etc).
These new DIA designs have joined the pre-existing spherical DIA cell design of Bill Durham as standard available DIA designs from the COMPRES project (Table 2).

6-8 assemblies
The series of COMPRES 6-8 assemblies that existed before 2012 covered a wide range of pressure and temperature. Two P-T regions were notably missing: the high-temperature region from 8 GPa to 14 GPa where the graphite furnace of our workhorse assembly (14/8 "G2" assembly) could no longer operate reliably due to the gradual loss of conduction in graphite, and the low-pressure/large volume region below 10 GPa.

The 14/8 High Temperature or "HT" assembly was developed to make up for the deficiencies in graphite heaters: a rhenium heater was used and the assembly was designed from scratch using thermal modeling codes (Hernlund et al., 2005) to optimize the dimensions for homogeneous thermal distribution in the sample. The sample diameter was reduced from 3.5 mm in the graphite heater version to 3.0 mm in the rhenium heater, thus there is a 36% volume penalty for attaining higher temperatures. The assembly was successful right away and has been popular for melting and other high-temperature experiments (up to 2300 °C) at pressures below 14 GPa.

The 18/12 assembly was developed by Emil Stoyanov at ASU over a period of several years, and was introduced as a COMPRES assembly once the development was complete. This assembly can achieve large volumes (sample diameter is 5 mm and length is 6.2 mm) at pressures up to 10 GPa and can also reach temperatures of 1800 °C or more in the pressure range where graphite can be used reliably (up to 7-8 GPa). It has also become popular recently as a large-volume workhorse assembly.

5-year plan for 2017-2022
(Advisors: Pamela Burnley, Lisa Danielson, Yanbin Wang, Paul Raterron, Matthew Whitaker)

DIA assemblies
DIA (a Japanese-designed sliding cubic anvil system) methods are increasingly important for deformation, ultrasonic and other types of multianvil experiments at synchrotron beam lines. One of the biggest issues in DIA assemblies is the difficulty of reliably measuring the temperature next to the sample. A partially related issue is producing the smallest possible thermal gradient in the sample region. Both of these become issues in the DIA designs because of the small space available, the tendency toward very thin furnaces that are disrupted by making holes for side-thermocouples, and the fact that buffer rods and back-reflecting layers (for ultrasonics) and pistons (for deformation) occupy the area that would be used for an axial thermocouple. These assemblies are run either with a thermocouple fairly far from the sample area, or in some cases with no thermocouple at all, meaning that a power calibration is relied on for temperature estimation.

This is obviously a difficult issue and it has not been fully solved to date. However, the solution of this problem, by developing a reliable thermocouple that is next to the sample and does not interfere with the furnace or with ultrasonic and deformation samples and assemblies, will be a primary goal of this cell assembly development effort over the next 5 years, now that the fabrication of DIA assemblies has become a routine part of the project.

Further developments to reduce thermal gradients are also targeted. In the ESRF assemblies, zirconia parts are used in place of some of the alumina parts, especially on the ends of the assemblies. Because zirconia is an excellent thermal insulator, this has reduced gradients in the central area where the sample is located. In the next 5 years we will work on strategically including zirconia in the assemblies (away from the x-ray path because it is also a high x-ray absorber) and will use thermal modeling to help in designing the pieces to reduce thermal gradients. Combined with the thermocouple improvements, this development can greatly improve the temperature measurement and control in the DIA assemblies.

Another development that would be useful would be to develop a more hydrostatic environment for deformation experiments. In the Griggs apparatus, liquid salt is used as a near-hydrostatic pressure medium. Stress can then be applied to a cylindrical sample from the ends, while maintaining hydrostaticity all around the sample. Technically for the stress tensor this means that sigma1 and sigma2 are equal with sigma3 being different. Molten salt presents some challenges in the Griggs machine in that it is very corrosive and the sample has to be sealed to survive. We currently do not know how to seal samples in the D-DIA and melting a salt confining media sleeve in the D-DIA disrupts the furnace. Thus a partial or complete redesign of the D-DIA will be undertaken to allow the use of molten salt or other very soft or liquid materials to confine the sample during deformation.

For GSECARS, there have been two retirements of senior technicians working on cell parts. It is more and more difficult to find a dedicated person, both in terms of personnel and in terms of budget. Thus the COMPRES Multi Anvil Development/Cell Assembly Project (MADCAP) effort will be called upon more than before to contribute to cell assemblies at GSECARS. The D-DIA cells are the most commonly used cells at GSECARS and the COMPRES project will collaborate on new developments of DIA cells at this beamline.

The ESRF group will also continue to use MADCAP standardized assemblies and to collaborate on new developments and designs.

Involvement of MADCAP in 3 different DIA efforts could eventually promote common designs and techniqueS shared across the groups which could help produce consistent results. This is especially likely when users cross over between platforms. This is expected to happen soon with the application of zirconia insulating parts in a D-DIA, which was introduced by the ESRF group, but will now be developed for the Stony Brook style DIA assemblies.

6-8 assemblies

A redesign of the COMPRES 18/12 assembly will be undertaken to eliminate asymmetric thermal gradients. We have recently discovered asymmetric thermal gradients in this assembly using a solid solution thermometer to map out thermal gradients. By asymmetric we mean that the gradients do not follow the expected cylindrical symmetry, because one of the electrodes in that assembly is placed off-center to allow for the insertion of the axial thermocouple. We plan

to make a new design where the off-center molybdenum electrode is replaced by a molybdenum ring centered along the axis. We will use thermal modeling for the dimensioning of the electrodes, and will test the thermal gradient in the new design using a solid solution thermometer to map out the temperature profile throughout the sample. A more isothermal, large sample will be the goal.
There is a group of standardized x-ray capable assemblies used in the GSECARS group. The cells for the T-25 (a 6-8 device, also referred to as the LVP) have been working out extremely well, which has led to the extension of the project to DIA cells as outlined above. Significant new development in 6-8 assemblies are still needed. One important advance will be to improve the transparency of the cells at low energy, by introducing low X-ray absorbing windows in the cells. This can be undertaken in the next 5-year period because we have stabilized the supply of cells which was the primary issue previously. Once the cells become easier to supply, further developments and improvements are achievable.

Additional cells to be developed for GSECARS will be for DELVE development, an effort led by Yanbin Wang to reach higher pressure using harder grades of carbide and smaller assemblies. These will be mostly 6/8 cells and will be designed for use up to 50 GPa, as outlined in the DELVE section of the COMPRES proposal. This is a considerable expansion of capabilities, with the current technology reaching about half of that pressure. This will require changes in designs due to the small cell sizes, and also the expected changes in some material behavior at the higher pressures that will require the use of new or modified materials for the cell parts. Another series of assemblies will be larger assemblies for the new large-volume press that is being proposed for location in the US. The MADCAP project will assist with development of these cell assemblies, regardless of where the press is located. These developments are expected to involve scaling up existing cell assemblies, as well as the inclusion of new capabilities to take advantage of the larger volume, such as fO_2 control.

Conclusion

MADCAP has been a successful community-based project of COMPRES since its inception. For the next five years, we propose a broad program of development of new cells for multi anvil work including new cells for use on synchrotron beam lines (DIA cells), for expanded pressure and temperature ranges in 6-8 multianvil devices, and for upcoming new technologies such as sintered-diamond multianvil methods and large-volume (5000-ton) multianvil approaches. We are committed to actively engaging the community of users to develop and then transition to standard usage a diverse suite of technologies, capabilites and assemblies that advances multianvil high pressure science.

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Table 1. Laboratories and people involved in the cell development effort in the current period of COMPRES (2012-2017)

Institution	**Location**	**Contact(s)/Advisors**
Aarhus University	Aarhus, Denmark	Martin Bremholm
Argonne National Laboratories, APS Sector 6	Argonne, IL	Matthew Whitaker, Haiyen Chen
Arizona State University	Tempe, AZ	Kurt Leinenweber
Australian National University	Canberra, Australia	Robert Rapp
Bayerishches Geoinstitut	Bayreuth, Germany	Dan Frost
Brown University	Providence, RI	Stephen Parman, Geertje Ganskow
Carnegie Institution of Washington, Geophysical Laboratory	Washington, D.C.	Haidong Zhang, Valerie Hillgren, Venkata Srinu Bhadram
Case Western Reserve University	Cleveland, OH	James Van Orman, Audrey M. Martin
China University of Geosciences	Wuhan, China	Zhenmin Jin
Chinese Academy of Sciences, Physics Institute	Beijing, China	Changqing Jin, L. Sun
Delaware State University	Dover, DE	Gabriel Gwanmesia
Florida International University	Miami, FL	Jiuhua Chen
IPGP	Paris, France	James Badro, Julien Seibert
Jacobs, located at NASA JSC	Houston, TX	Lisa Danielson
Jilin University Superhard Materials	Changchun, China	
Lehigh University	Bethlehem, PA	Kai Landskron
Los Alamos National Laboratories	Los Alamos, NM	Jianzhong Zhang
Macquarie University	Sydney, Australia	George Amulele
Massachusetts Institute of Technology	Cambridge, MA	Bill Durham
NASA Johnson Space Center	Houston, TX	Lisa Danielson
National Cheng Kung University	Tainan, Taiwan	Jennifer Kung
Renmin University	Beijing, China	
Rice University	Houston, TX	KyuseiTsuno
Seoul National University	Seoul, Korea	Eun Jung Kim

Stony Brook University	Stony Brook, NY	Baosheng Li, Xuebing Wang
Texas A&M University	College Station, TX	Caleb Holyoke, Zhicheng Jing
Universite Lille (and ESRF)	Villeneuve d'Ascq, France	Paul Raterron, NadègeHilairet
University of Amsterdam	Amsterdam, The Netherlands	Wim van Westrenan
University of California at Davis	Davis, CA	Charles Lesher
University of California San Diego, Scripps Institute of Oceanography	San Diego, CA	Anne Pommier
University of Chicago,GSECARS	Argonne, IL	Yanbin Wang, Tony Yu
University of Hawaii	Honolulu, HI	Bin Chen
University of Michigan	Ann Arbor, MI	Jie (Jackie) Li
University of Minnesota	Minneapolis, MN	Jed Mosenfelder
University of Nevada at Las Vegas, Dept of Geoscience	Las Vegas, NV	Pamela Burnley
University of Nevada at Las Vegas, HiPSEC /Dept. of Physics & Astronomy	Las Vegas, NV	Liping Wang
University of Western Ontario	London, Ontario, Canada	Richard A. Secco, Wenjun Yong
Vrije University	Amsterdam	Edgar Steenstra
Yanshan University, State Key Lab of Metastable Materials	Qinhuangdao, China	Dongli Yu

Table 2: Examples of Multi-anvil assemblies developed and standardized by the COMPRES Multi-Anvil Development/Cell Assembly Project

Assembly name	**Peak pressure**	**Peak temperature**	**Design**
6/8 type assemblies			
8/3	25 GPa	2319 °C	Rhenium furnace
10/5	20 GPa	2000 °C	Rhenium furnace
14/8 “G2”	13 GPa	1200 °C	Graphite box furnace
14/8 step heater	15 GPa	1400 °C	Graphite step furnace
14/8 “HT”	15 GPa	2200 °C	Rhenium furnace
18/12	9 GPa	1500 °C	Graphite box furnace
8/3 window assembly in-situ	25 GPa	2200 °C	$LaCrO_3$ sleeve and rhenium furnace with windows
10/5 window assembly *in-situ*	20 GPa	2200 °C	$LaCrO_3$ sleeve and rhenium furnace with windows

10/5 equatorial assembly *in-situ*	20 GPa	1700 °C	TiB_2+BN or C furnace, MgO equatorial window, mullite octahedron
14/8 "G2" *in-situ*	13 GPa	1200 °C	Graphite box furnace, forsterite sleeve
14/8 equatorial assembly *in-situ*	15 GPa	1500 °C	TiB_2+BN step furnace, MgO equatorial window, mullite octahedron
DIA-type assemblies			
Spherical D-DIA assembly	6 GPa	1700 °C	Based on Durham sphere and cradle idea
D-DIA (Deformation DIA)	8 GPa	1400 °C	Stony Brook design made at ASU
U-DIA (Ultrasonic DIA)	8 GPa	1400 °C	Stony Brook design made at ASU
DIA (regular DIA for diffraction)	8 GPa	1400 °C	Stony Brook design made at ASU
ESRF 9 mm assembly	8 GPa	1400 °C	Paul Raterron and Nadege Hilairet design

6. NSLS-II Beamline Frontier Infrared Spectroscopy (FIS) Facility for Studies under Extreme Conditions (PIs: Russell Hemley, Zhenxian Liu, GWU)

Introduction

The coupling of the diamond anvil cell and synchrotron techniques has greatly promoted the progress and breakthroughs in the development of ultrahigh-pressure diamond-anvil cell techniques in the past several decades, in particular the synchrotron based infrared spectroscopy under extreme conditions as diffraction limited spatial resolution is essential. With the funding support through COMPRES since 2002, the infrared diamond anvil cell (IR-DAC) facilities at the National Synchrotron Light Source (NSLS-U2A) became an important and unique resource for the COMPRES user community. Combined synchrotron infrared micro-spectroscopic techniques, Raman scattering, and visible spectroscopy with diamond- and moissanite-anvil cell methods, U2A was the first dedicated high-pressure synchrotron IR beamline in the world and a COMPRES showcase for the worldwide earth science and high-pressure research communities. We significantly broadened our user base and provided convenient access for users from the COMPRES community. In addition, we facilitated and supported user research projects on a broad range of problems in high-pressure geoscience and planetary science, complemented by studies in materials science, condensed matter physics, chemistry, and biology. The legacy of success of the high-pressure IR user programs at NSLS made a strong case to develop the Frontier Synchrotron Infrared Spectroscopy Beamline under Extreme Conditions (FIS) at NSLS-II with over $2M committed from the NSLS-II FY16 operations funds to procure the storage ring optical extraction system and construction of the lab space (beamline cabin) on the NSLS-II experimental floor in 2016. This will open new opportunities for the geoscience community to take the advantage of the state-of-the-art IR facilities at NSLS-II. The continuing funding support through COMPRES-IV will enable us to extend the high-pressure IR programs and to guarantee continued access for the COMPRES user community to the brightest and most stable synchrotron IR source in the world, allowing scientists to address key problems ranging from outer solar system bodies to the Earth's core.

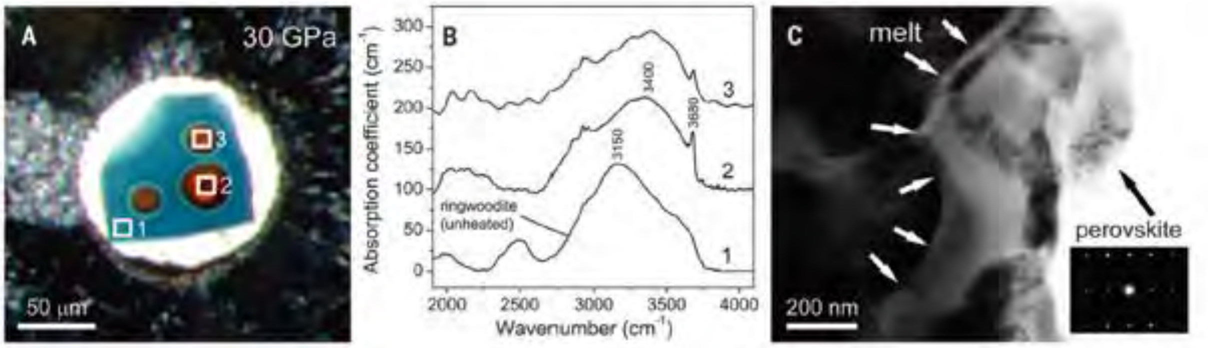
The legacy of success at NSLS-U2A

High-pressure spectroscopy provides essential and often unique information about the properties of materials under extreme conditions. In particular, vibrational infrared (IR) spectroscopy provides detailed information on bonding properties of crystals, glass, and melts, thereby yielding a microscopic description of thermochemical properties. Infrared measurements also provide information on electronic excitations including crystal-field, charge-transfer, excitonic spectra of insulating and semiconducting materials, and pressure-induced metallization of insulators. Such information is crucial for developing a comprehensive understanding of the structure, dynamics, and evolution of planetary interiors.

Synchrotron radiation is an ideal source for IR studies to probe microscopic samples including *in situ* measurements under extreme conditions due to its high brightness, broad-spectrum distribution, and diffraction-limited performance. The National Synchrotron Light Source (NSLS) had the unique capability to provide synchrotron radiation over a broad range from hard x-ray down to the very far IR. The IR radiation at the VUV ring of the NSLS had world-class performance with up to $\sim 10^4$ times the brightness of a conventional thermal (lamp) source. Initiated by our group in 1990, the high-pressure IR program at NSLS became an important complement for the high-pressure user community. Later on, as one of the six IR beamlines at the NSLS, U2A became the first dedicated high-pressure synchrotron IR facility in the world, with the capacity for synchrotron IR micro-spectroscopic techniques, Raman scattering, and visible spectroscopy combined with diamond-anvil cell methods for the measurement of far- to near-IR and visible spectra of materials from ambient to ultrahigh pressures at variable temperatures. The beamline was built and has been managed by us since 1998 and became available for general users in 2000. NSF-COMPRES has been the major funding source for the beamline operation as well as facility major upgrades in 2010. The high-pressure IR program at the NSLS has been very successful in terms of beamline development, outreach of user community, and scientific productivity. A number of important scientific and technical challenges were being addressed at the facility, making it a highly attractive complement to x-ray sources for high-pressure studies. Here are few recent highlights:

Dehydration Melting at the Top of the Lower Mantle [1]

The high water storage capacity of minerals in Earth's mantle transition zone (410 to 660 kilometer depth) implies the possibility of a deep H_2O reservoir, which could cause dehydration melting of vertically flowing mantle. A synergetic effort led by B. Schmandt (University of New Mexico) and S. Jacobsen (Northwestern) to employ multiple techniques including synchrotron IR spectroscopy, TEM, seismic P-to-S conversions recorded by a dense seismic array in North America, and numerical modeling to examined the effects of downwelling from the transition zone into the lower mantle. In experiments, the transition of hydrous ringwoodite to perovskite and (Mg,Fe)O produces intergranular melt. The advanced synchrotron IR micro-spectroscopy with high spatial resolution up to the diffraction limit provided key diagnostic of the water content in laser-heated sample area quenched from extreme high P-T conditions equivalent the lower mantle environment. Detections of abrupt decreases in seismic velocity where downwelling mantle is inferred are consistent with partial melt below 660 kilometers. The discovery suggests water from the Earth's surface can be driven to such great depths by plate tectonics, eventually causing partial melting of the rocks found deep in the mantle. These results will help scientists in understanding how the Earth formed, what its current composition and inner workings are and how much water is trapped in mantle rock.

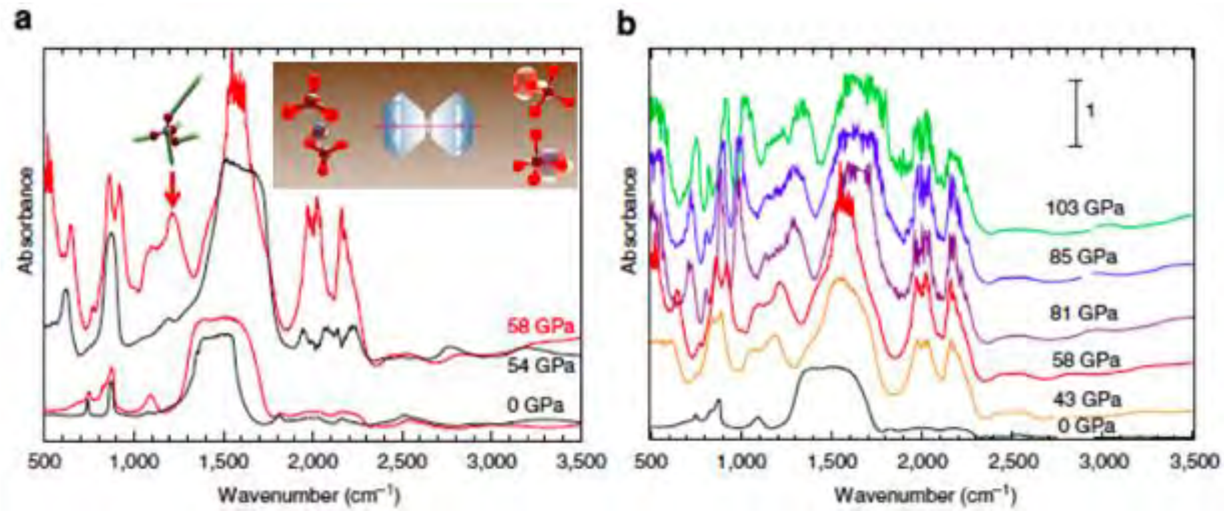


Laboratory experiments on hydrous ringwoodite. (A) Single-crystal of hydrous ringwoodite (blue crystal) containing 1 wt % H_2O inside a DAC at 30 GPa. The sample was laser heated to 1600°C in several spots (orange circles) to perform direct transformation to perovskite and (Mg,Fe)O. (B) Synchrotron-FTIR spectra of the recovered sample in three locations: an unheated part of the crystal (spectrum 1) and two locations within laser-heated spots (spectra 2 and 3). FTIR spectra were collected with a 10 µm by 10 µm aperture, illustrated and numbered by white boxes in (A). (C) TEM within a laser-heated spot (position 2) shows crystals of perovskite and intergranular amorphous quench (melt).

New Carbon Bonding under Extreme Conditions [2]

Only a small fraction of our planet's total carbon is found at the surface. In fact, Earth's mantle is thought to be the largest carbon reservoir. Carbonates, and in particular ferromagnesite ($(Mg,Fe)CO_3$), are likely candidates for deep-Earth carbon storage and therefore play a key role in the deep carbon cycle. The behavior of these carbonates at the high pressure and temperature conditions of Earth's interior is therefore of great interest for understanding global carbon cycling and storage. A new study led by E. Boulard (Stanford University) found unequivocal experimental evidence for tetrahedrally coordinated carbon in high pressure carbonates, obtained by combined synchrotron IR studies at U2A beamline, and theoretical calculations at University of Chicago. With the combination of *in situ* synchrotron IR spectroscopic measurements carried out at high pressure, and *ab initio* calculations on the ferromagnesite structure, it was possible to identify a unique vibrational signature present only in the high-pressure phase, and thus a new carbon-oxygen bond forms in ferromagnesite under high pressure and temperature. The new vibrational signature is assigned to tetrahedrally coordinated carbon atoms with asymmetric C-O bonds.

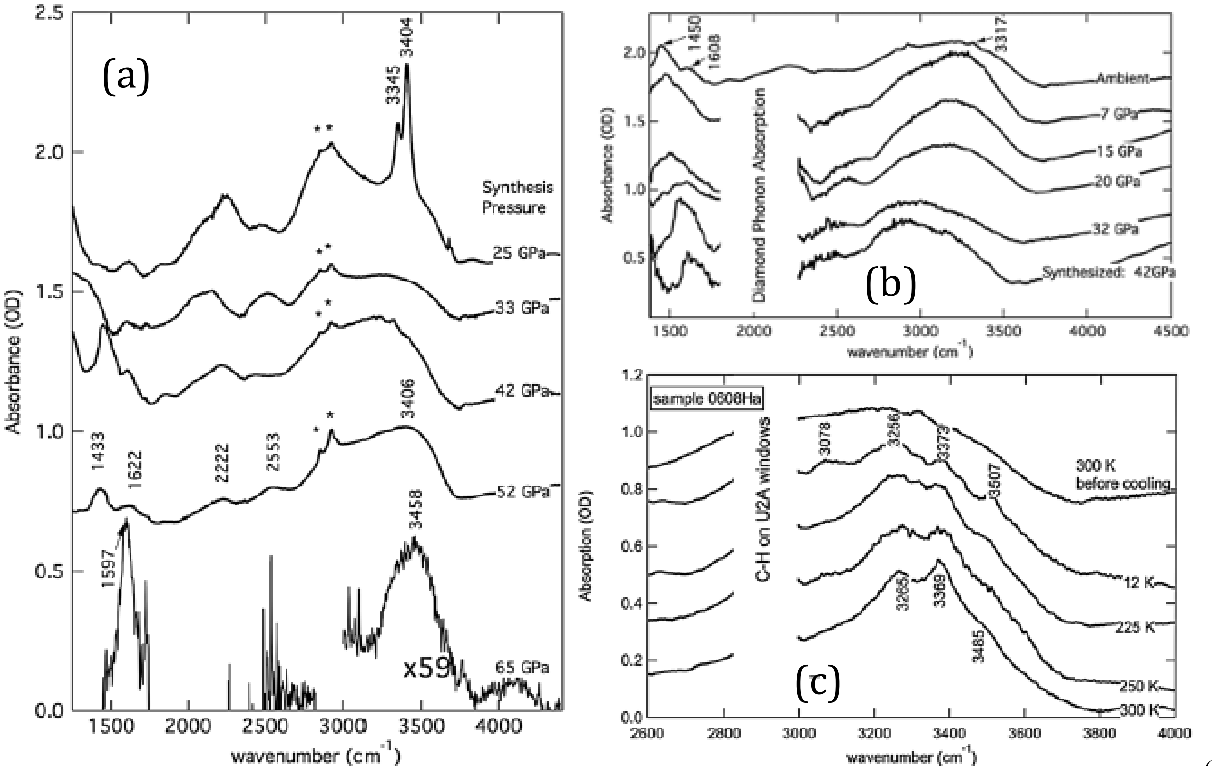
Ferromagnesite represents an important rock-forming mineral, fundamentally distinct from silicates in Earth's crust. At low pressure, carbon bonds to three oxygen atoms, while silicon bonds to four. Tetrahedrally coordinated carbonates likely exhibit dramatically different behavior compared to three-fold coordinated carbonates, including altered reactivity with other mantle phases and changes in chemical melt properties. This bonding behavior could therefore have significant implications for carbon reservoirs and fluxes, as well as for our understanding of the global geodynamic carbon cycle.



In-situ synchrotron IR measurements at high pressure. (a) Experimental IR spectra collected on compression of the ferromagnesite (black lines) at 0 and 54 GPa, and on decompression of the post-magnesite phase (red lines) at 58 and 0 GPa. The region between 1900 and 2300 cm^{-1} is dominated by absorption from the diamond anvils. The inserts show carbon environment and the vibrational mode at ~1252 cm^{-1} (marked by the arrow) identified as a unique signature of the high-pressure phase. (b) Experimental IR spectra collected on the decompression of the post-magnesite phase from103 to 0 GPa. The scale bar indicates the optical density.

Dry (Mg,Fe)SiO_3 Perovskite in the Earth's Lower Mantle [3]

The water content of the lower mantle is uncertain, yet it has far-reaching impacts on the physical behavior of the mantle and our planet's evolution. Small amounts of dissolved water in the major nominally anhydrous silicates of the upper mantle, including the transition zone, are shown to have significant effects on the mantle's deformation, elastic moduli, and relaxation. Further, the incorporation of water in olivine polymorphs increases the reaction kinetics of phase transformations with implications for deep-focus earthquakes and mass transfer across the base of the transition zone. The transition zone has a large water storage capacity; that is, it can incorporate 1-2 wt% H_2O before inducing melting, in which the major carriers of water in the transition zone are the olivine polymorphs, wadsleyite, and ringwoodite. Recent evidence from deep diamond suggests that at least portions of the transition zone contain up to 1 wt % H_2O.



(a)

Zero-pressure IR spectra of perovskite synthesized from 3941 as a function of synthesis pressure. For comparison, the lower curve is the IR spectrum of 1009Da (14,516 starting sample) vertically expanded by a factor of 59 (the ratio of OH content of the two starting samples). The sharp peaks (*) are due to C–H on the optical system. (b) Decompression of sample 0608Ha laser heated at 42 GPa in an argon pressure medium to ambient pressure. No major changes in features are observed, with a negative shift of the main OH band with a slope of ~4.2 cm^{-1}/GPa. Additional bands in the O–HO bending region have a positive shift with the 2216 cm^{-1} band with a +12.3 cm^{-1}/GPa, 1444 cm^{-1} and 1564 cm^{-1} peaks with relatively weak shifts of +2.4 cm^{-1}/GPa, and +2.6 cm^{-1}, respectively. (c) IR spectra of sample 0608Ha cooled to 12 K at 10^{-6} torr after synthesis and recovery. Four peaks become evident below 100 K, and three peaks are retained upon returning to room temperature.

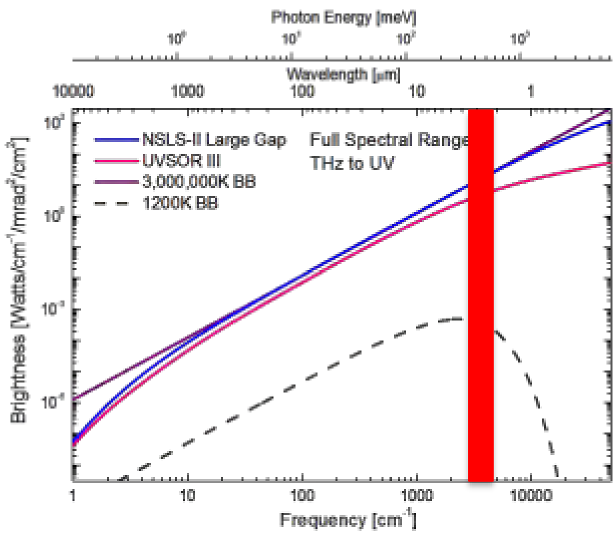
For the lower mantle, however, hydration of the ABO_3 rare earth perovskites (A^{2+} and B^{4+} cations) shows that significant hydration with as much as 2 wt % H_2O can occur with B-site aliovalent substitutions at temperatures above 1300 K. These proton conducting, acceptor-doped perovskites accommodate the aliovalent cation via oxygen vacancies, such that many of these solid oxide fuel cell materials are significantly oxygen deficient. Combined synthesis experiments and first-principles calculations, a team led by W. Panero (Ohio State University) found that $MgSiO_3$-perovskite with minor Al or Fe does not incorporate significant OH under lower mantle conditions. Perovskite, stishovite, and residual melt were synthesized from natural Bamble enstatite samples (Mg/(Fe + Mg) = 0.89 and 0.93; Al_2O_3<0.1 wt % with 35 and 2065 ppm weight H_2O, respectively) in the laser-heated diamond anvil cell at 1600~2000 K and 25~65 GPa. Combined synchrotron IR spectroscopy, x-ray diffraction, and ex situ transmission electron microscopy analysis demonstrates little difference in the resulting perovskite as a function of initial water content. Four distinct OH vibrational stretching bands are evident upon cooling below 100 K (3576, 3378, 3274, and 3078 cm^{-1}), suggesting four potential bonding sites for OH in perovskite with a maximum water content of 220 ppm weight H_2O, and likely no more than 10 ppm weight H_2O. Complementary first-principles calculations on the Fe-free material predict multiple potential bonding sites for hydrogen in perovskite, each with significant solution enthalpy (0.2 eV/defect). The calculations also reveal that perovskite can dissolve less than 37 ppm weight H_2O (400 ppm H/Si) at the top of the lower mantle, decreasing to 31 ppm weight H_2O (340 ppm H/Si) at 125 GPa and 3000 K in the absence of a melt or fluid phase. These results resolve a long-standing debate of the perovskite melting curve and explain the order-of-magnitude increase in viscosity from upper to lower mantle.

These highlights demonstrate the needs of the capacity of synchrotron IR spectroscopy under extreme *P-T* conditions for the COMPRES community.

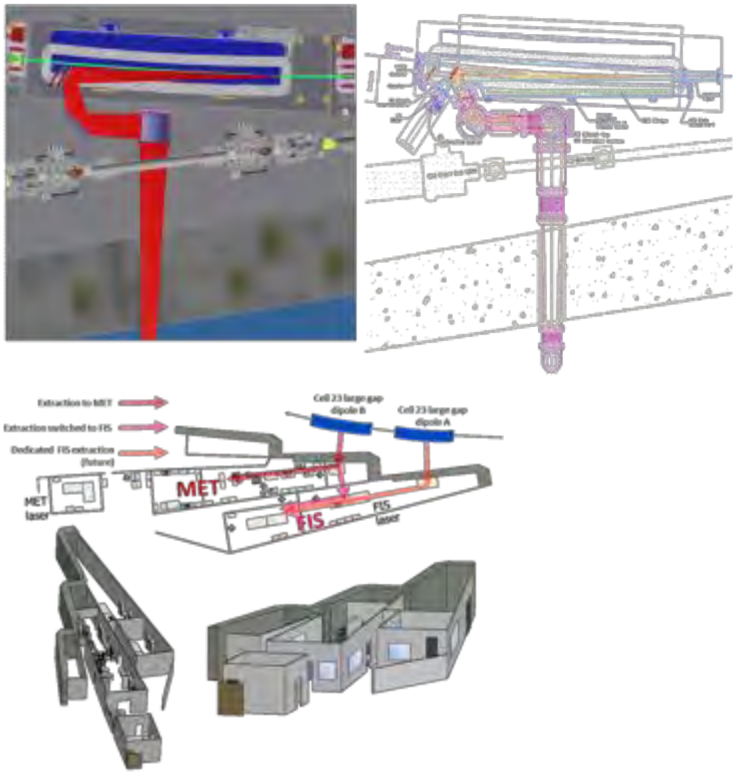
The Frontier Infrared Spectroscopy (FIS) Beamline at NSLS-II

As NSLS ceased its operation on September 30, 2014 and NSLS-II achieved "first light" on October 23, 2014, the high-pressure IR facility/programs are currently moving forward from NSLS to NSLS-II with anticipated brighter and more stable synchrotron IR radiation beam. Because of the successful high pressure IR program with growing user community and beamtime demands at NSLS, the Frontier Synchrotron Infrared Spectroscopy (FIS) Beamline under Extreme Conditions, the successor to NSLS-U2A, was selected as one of the five BDN beamlines developed by NSLS-II. It is currently under development and will be the first synchrotron IR beamline at NSLS II. FIS and Magnetic, Ellipsometric & Time-resolved (MET) Infrared Spectroscopy will share the first synchrotron beam from a bending magnet source at NSLS-II. The FIS program will serve the scientific communities studying materials under extreme P-T conditions and the MET program will serve primarily the condensed matter physics and materials science communities for the study of electronic behaviors in solids. Both programs depend on the very high brightness and broadband IR light produced in the dipole bending magnets of the NSLS-II electron storage ring to achieve diffraction-limited performance in order to overcome the severe throughput limits of diamond anvil cells (DACs), ellipsometers, and inherently small samples. The spectral range includes the very far-IR, which is crucial to study novel behavior such as insulator-metal transitions, superconductivity, ferroelectricity and magnetism, as well as materials ranging from semiconductors and metals, energetic materials, high-explosives, plastics, and complex composites.

To meet these needs, NSLS-II is developing the first beamline to extract IR from cell 23, one of the special, large-gap dipole bending magnets. These particular magnets avoid cutoff effects that would nominally cause very poor long-wavelength performance, and are arranged in pairs at three locations around the storage ring. Based on the designed storage ring current of 500 mA, top-up injection and the overall ultra-high stability of the facility, the performance estimates indicate that NSLS-II will be world-leading in terms of brightness and signal-to-noise over the widest possible spectral range – including the very far-IR. Most importantly, NSLS-II has already committed \$2M from its FY16 operation funds for two major items including the dipole chamber, UHV extraction and transport and construction of the end-station laboratory space (beamline cabins) on the NSLS-II experimental floor in 2016, a crucial step to relocate all end-station equipment and new technical developments ready for science commissioning on day one when the IR beam extracted and delivered to the IR beamline cabin. The project on developing FIS at NSLS-II represents a great cost-efficient model as a joint effort by NSLS-II and COMPRES. The total cost for the first synchrotron IR beam extraction and construction of the beamline cabins is over \$5M, fully covered by NSLS-II. On the other hand, the investment by NSF-COMPRES for beamline operations and technical developments over the years made the high-pressure synchrotron IR facilities state-of-the-art at NSLS and NSLS-II. Overall, the design capabilities of NSLS-II with its smaller source size, higher brilliance, and broader spectral range ideally match the materials research under extreme *P-T* conditions through the coupling of the DAC techniques. The execution and realization of FIS will provide superior capabilities to continuously accommodate the growing user demand and further expand the high-pressure IR research at the NSLS-II dedicated to the study of materials under extreme pressure and temperature (*P-T*) conditions.



Calculated brightness of the synchrotron IR radiation extracted from the NSLS-II large-gap dipole-bending magnet compared to the IR sources at UVSOR III in Japan, 3000000K, and 1200K black body sources. It is expected to be world-leading synchrotron IR source with widest spectral range and 10~1000 better stability (less noise). In particular, it has gain by a factor of ~5 in the O-H and H-H stretching vibration region, crucial for studies on hydrous, nominally anhydrous minerals and hydrogen under extreme P-T conditions equivalent to those conditions in transition zone and lower mantle or giant gas planets.



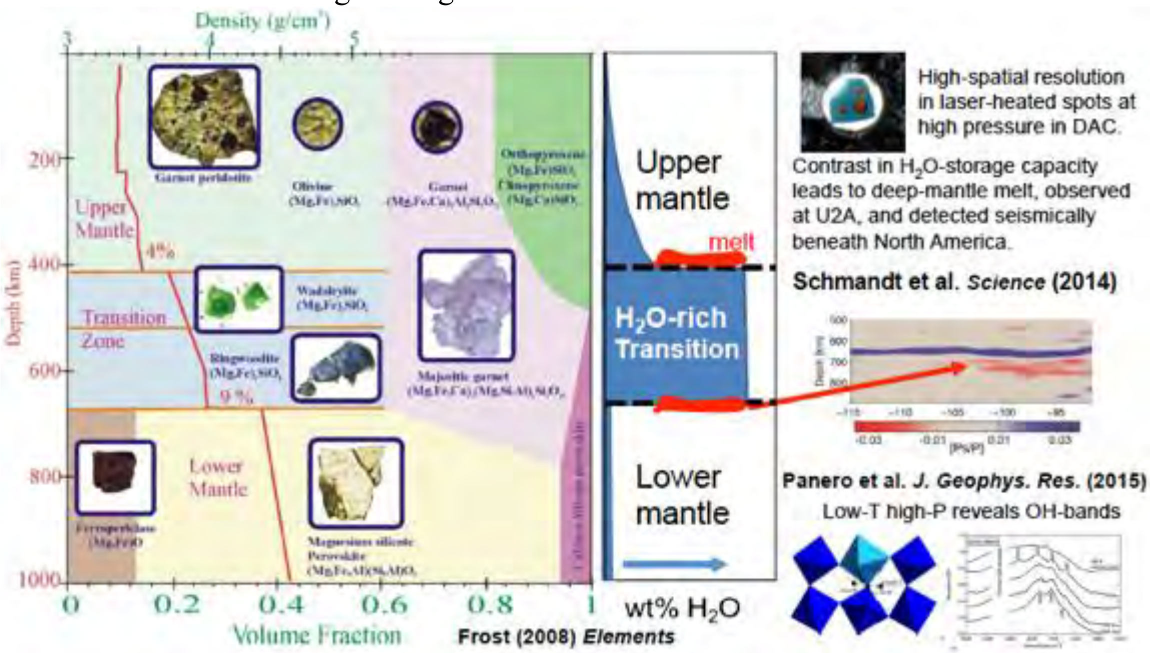
Schematic of FIS/MET large gap dipole extraction (left and middle) and the beamline cabins on experimental floor (right). Current plan/configuration provides an option to add second large-gap dipole extraction from bending magnet 23BM-A when funds available in the future. This will make both FIS and MET operate independently and double the current user beam time. Significant cost saving will be achieved on beam extraction design and fabrication.

Major steps of current schedule are shown as below:
April 2016: Awarded Dipole Chamber, UHV extraction and Transport;
May 2016: Resume procurement and construction of FIS/MET instrument space in 22ID and 22BM experimental floor areas;
May 2017: Beneficial occupancy of FIS/MET experiment space, begin installation of spectrometers and other instruments;
Nov. 2017: Installation of UHV systems through shield wall;
Jan. 2018: Integrate Systems;
May 2018: Commissioning, followed by Operations.

New techniques and opportunities at FIS for the high-pressure user community

The FIS facility at NSLS-II will provide brighter, more stable, and broader synchrotron source spanning from THz, far-IR, up to UV. The experimental floor space will be expended more than four times larger than the area at NSLS-U2A. This will allow us to develop new techniques, including combined laser-heating DACs with FTIR spectroscopy for *in-situ* high P-T studies, time-resolved method with step-scan, and pulsed beam for studies under dynamic compression, as well as to add new equipment and improve existing techniques. These developments and techniques implemented at FIS will provide opportunities and access for the high-pressure user community to address numerous scientific questions in Earth and planetary science and beyond:

In-situ high P-T IR spectroscopic techniques and studies of Earth's deep water cycle
IR spectroscopy provides a key and often-unique experimental approach due to its high sensitivity to volatile components (e.g, O-H bonds and molecular components) and potential diffraction-limited spatial resolution. As such, it serves as an invaluable tool for evaluating the behavior of hydrous and nominal anhydrous minerals at high *P-T* conditions as well as during cooling.



Earth's deep water cycle: all samples (left) synthesized at high P-T, quenched and measured the water content at ambient conditions. Resulted obtained at NSLS-U2A shown in the highlights provide new insights on water storage capacity and melt generation.

It is essential to extend diamond anvil cell techniques to higher temperatures and pressures with combined external [4-5] and laser heating techniques in order to directly probe thermodynamics, chemical diffusion, and molecular coordination under high *P-T* conditions. This requires brighter sources with diffraction-limited performance and superior stability in the IR range. The capacity of the large-gap dipole at NSLS-II will provide an ideal IR source for such studies to couple the high *P-T* DAC techniques with the FTIR spectroscopic measurements and to address these scientific questions and challenges related to Earth and Planetary Sciences. An important class of problems to be addressed thus includes the following:

a) Is the mantle is a reservoir for potentially vast quantities of volatiles, and what are all the possible hydrous and nominally anhydrous phases in which water could be retained at depth? The answer to this fundamental question will involve phase equilibrium and saturation experiments over a broad range of pressures, temperatures, and compositions.
b) How is water distributed in Earth's interior and how does it cycle from great depths to the surface? Why has the ocean mass fluctuated so little in the past, thereby allowing the evolution of life on Earth?
c) What subduction zone minerals can retain water and carbon until they are in the transition zone where they can be readily absorbed by minerals there?

d) When mantle rocks rise above 410 km depth, do saturated minerals dehydrate, thus releasing dense aqueous melts that are recycled to depth at mantle downwellings? That is, is the 410 km seismic discontinuity a dehydration boundary or "water filter"?
e). How do small amounts of water affect the rheologic properties of high-pressure minerals and the patterns of convection in the deep Earth?
f). How do small amounts of water affect the concentration (and mobility) of point defects and hence electrical conductivity?

Planetary Science and Materials Science
Materials in extreme *P-T* environments present a fertile, unexplored ground for unexpected scientific discoveries that will significantly impact energy science. A myriad of unexpected discoveries have emerged from virtually any substance studied over a significant *P-T* range. Simple elements such as H_2 [6, 7], and O_2 [8-11] show 5 to 10 new high *P-T* phases; the number is considerably higher for compounds. For instance, after centuries of studies of H_2O [12], close to two dozen stable [13-15] and metastable [16] phases of liquid, solid [17, 18], and amorphous [19] ices have been discovered under extreme *P-T* conditions. In the pressure dimension, creation of novel materials becomes the rule rather than the exception. Conceivably, an order of magnitude more materials could be discovered in extreme *P-T* environments compared to all materials now known to exist at ambient conditions. Spectroscopy is an invaluable and sometimes unique probe that can be used to study *in-situ* properties such as structures and chemical bonds of these materials under extreme *P-T* conditions. Here we give a few specific examples of science themes that are well suited to FIS:

Nano-crystalline materials and porous materials. Nanophase and composite materials have novel physical and chemical properties compared to their bulk counterparts due to a large fraction of surface or inter-surface atoms, which complements bulk crystalline materials and exhibit enhanced performance over a broad range of extreme *P-T* conditions. These materials have potential for future applications in energy efficiency, production, and storage. The high *P-T* nanoscience opens new areas for discovery of novel materials and nanoscale phenomena. Recent studies on BN nanotubes at high-pressure reveal a novel pressure induced phase transition in such two dimensional materials [20]. In addition, porous materials, such as zeolites/natrolites, have hydrated framework alumosilicates which comprise an important class of low–density materials. Their frameworks are composed of corner connecting $(Al, Si)O_4$ tetrahedra, yielding cavities and channels of molecular dimensions. Combined synchrotron IR spectroscopy and Raman scattering studies show new phenomena and potential applications of energy storage and CO_2 sequestration [21, 22]. One of the main goals of high-pressure spectroscopic studies in this area will be *in-situ* probing of the evolution of the chemical bonding and possible solid-solid phase transformations and other physical parameters under extreme *P-T* conditions.

Chemical reactions and kinetics under extreme conditions. The chemistry of materials under high *P-T* extreme conditions is one of the most important areas in materials science. This includes the high *P-T* chemistry of explosives, metals in contact with reactive low-*Z* materials such as H_2 and H_2O, and complex composites (*i.e.*, interfaces), all of which may change appreciably as materials age. Pressure-induced reactions between Fe and H_2 (and H_2O) have been characterized to megabar pressures, and new high-pressure hydrides have been found even at 300 K [23]. These early studies can now be extended to a broader range of conditions (*i.e.*, high *T*) as well as to different metals. To better understand and design complex chemical reactions, it is crucial to directly and accurately monitor the evolution of bonding, molecular coordination and separation, diffusion, reaction rate, and detailed chemical kinetics at high *P-T* conditions. High-pressure IR spectroscopy combined with the unique pulsed synchrotron source will be one of the *in-situ* probes used to follow chemical reactions and provide deep insight into reaction kinetics and reaction mechanisms.

Synthesis, recovery and characterization of new materials. Research at extreme conditions provides new insight into the synthesis of materials with properties important for industrial, technical and scientific applications [24]. These include super hard materials, high-temperature superconductors, ferroelectrics, multiferroics, high energy density materials, hydrogen storage materials, and nano-materials. The thermodynamic properties and electronic structures serve to determine a material's phase diagram, which in turn yields valuable insight in the search for new materials having desirable properties. Materials generated at extreme conditions need to be recovered if they are to be useful for real-world applications, and this can be a challenging process. This may include approaches such as improving the technology, making the extreme environment more attainable and affordable. For instance, the hydrogen-rich, environmentally clean, hydrate presents an example of metastable recovery through *P-T* and chemical paths. Two hydrogen hydrates $H_2(H_2O)$ and $H_2(H_2O)_6$ were discovered at 2 GPa [25]. In an attempt to recover the hydrate at low temperature, a new $H_2(H_2O)_2$ sII clathrate was discovered at 0.2 GPa and recovered at ambient pressure well above liquid nitrogen temperature [26-28]. Since fundamental understanding of chemical bonding and kinetics is crucial to recover novel materials from extreme conditions, high-pressure spectroscopy including synchrotron IR spectroscopy combined with cryogenic techniques can be employed to investigate mechanisms to recover clathrates for real world energy storage applications.

Energetic and other organic materials at extreme conditions. Understanding the behavior of energetic materials under extreme conditions is crucial for gaining insight into their kinetics when a shockwave (a condition of high *P-T*) passes through and detonates them. Vibrational spectroscopies such as IR and Raman are valuable tools for gathering information about intra- and inter-molecular bonding alterations of the molecules under such extreme conditions. Studies of explosives under static high-pressure can be conducted in a DAC with variable temperatures. In contrast to other techniques, synchrotron IR spectroscopy does not damage energetic materials such as TATB [29] and FOX7, both of which are extremely sensitive to visible laser light. Moreover, it has diffraction-limited spatial resolution down to very far-IR region and provides phonon modes related to lattice vibrations. It is also complementary to Raman spectroscopy, yielding a comprehensive spectroscopic picture of the materials when subjected to extreme conditions. There are also ongoing efforts to perform IR measurements on mixtures of the decomposition products of explosives (e.g. nitrogen and water) aimed at achieving a better understanding of the effect of AB mixtures on altering intramolecular and intermolecular potentials.

Overall, FIS at NSLS-II will serve as a unique facility for the COMPRES user community, and will help to broaden to the high-pressure community. The requested funds will allow us to not only maintain the routine beamline operation but also continue to develop the advanced techniques such as external and laser heating DAC techniques for *in situ* spectroscopic studies under high *P-T* extreme conditions, time-resolved IR spectroscopic methods for studies under dynamic compression or fast cooling to tackle these key questions and challenges for the user community throughout the COMPRES IV period and beyond.

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7. NSLS-II XPD & APS 6BM-B Beamlines MAP (PI: Don Weidner, Stony Brook)

Introduction
In this last decade, the greatest growth in multi-anvil research capabilities have come in our ability to characterize mechanical properties of Earth materials at elevated pressure and temperature. This research thrust has been led by COMPRES facilities and has been enabled by the combination of multi-anvil technology and synchrotron x-rays. In this proposal we outline a program to continue development and implementation of this research area. We propose a one year continuation of the COMPRES program utilizing a white beam at beamline BM6B at the Advanced Photon Source (APS), and a five year program utilizing a monochromatic beam at the National Synchrotron Light Source II

(NSLS II). The APS beamline is a white beamline that is setup with a DDIA or a Rotational Drickamer Apparatus (RDA) in a 200 ton press. We share the time on this beamline with a materials program engaged with white beam x-ray diffraction. The COMPRES program receives over half of the time. This beamline was created at the closing of the highly productive multi-anvil beamline at the NSLS. The APS program continues the work that was begun at the old NSLS. Before its closing in 2014, we received about 20 proposals for research per trimester. Since we opened the new beamline at the APS, we have recovered about 2/3 of the user pressure. At this time we are constructing a multi-anvil end station at the NSLS II. The monochromatic beamline is in the D hutch of the powder diffraction beamline, XPD, which receives high energy x-rays from a damping wiggler. We will be able to operate either a DT25 guideblock or a DDIA in a 1000 ton press in this beamline. While beamtime will be limited at this station, we anticipate that we will be able to conduct our full range of experiments at pressures and temperatures into the lower mantle.

These beamlines continue to address an exciting research agenda. Here we outline some of the current research focus. The NSLS II program will use a new guideblock, with higher pressure capabilities that should be able to reach into the lower mantle. While beamtime will be more restricted by competition, we expect this program to make new excursions into regions of the Earth that have not previously been explored experimentally.

Scientific Program

Our understanding of the makeup and evolution of the Earth is strongly tied to our understanding of the materials that comprise the Earth. Pressure and temperature set the environment where these minerals and melts are found, and it is the goal of high-pressure experimental studies to probe and characterize Earth material systems. A 2008 workshop on seismological research frontiers *(Seismological Grand Challenges in Understanding Earth's Dynamic Systems, 2009)*, funded by the National Science Foundation (NSF), considered promising research directions for the next decades and identified 10 Seismological Grand Challenge research questions including: *How do faults slip?; How does the near-surface environment affect natural hazards and resources?; What is the relationship between stress and strain in the lithosphere?; Where are water and hydrocarbons hidden beneath the surface?; How do magmas ascend and erupt?; What is the lithosphere-asthenosphere boundary?; How do plate boundary systems evolve?; How do temperature and composition variations control mantle and core convection?;* and *How are Earth's internal boundaries affected by dynamics?* While these questions drive the agenda of the next decade seismology research, their answers require an in depth understanding of the mechanical properties of Earth materials.

Elasticity

The most robust fingerprint of the chemical and thermal state of the Earth's interior are the elastic properties of Earth materials. Radial variations in seismic velocity point to phase transitions, melting, and general pressure increase. These transitions require a comprehensive understanding of the elastic properties of materials as a function of all of the relevant variables. The last few years has seen tremendous growth in our data base as well as our experimental tools for defining this information. The interpretation of seismological profiles of Earth's interior has long been the principal motivation for measuring the acoustic velocities and the elastic tensors of minerals, both at ambient and high P or T conditions. As the resolution of seismological studies continues to improve, the need for more and better elasticity data, under simultaneous high pressures and high temperatures, increases. Two specific challenges that can be highlighted include: the interpretation of seismic anisotropy throughout the planet, from uppermost mantle to inner core conditions; and understanding lateral variations of compressional and shear wave velocities (∂Vp and ∂Vs) in terms of composition and/or temperature variations. These goals require the mineral physics community to provide complete characterization of elastic anisotropy, as well as aggregate acoustic velocities, in minerals, and also the variation of these properties with pressure, temperature, and composition. Simultaneous ultrasonics + XRD investigations in the multi-anvil press permit the EoS and acoustic properties of minerals to be evaluated under high-P,T conditions. The multi-anvil beamline at the NSLS has been the pioneer of such measurements and continues to develop a wider array of possible samples for such high P-T experiments[1-35]. An example is the study of $MgSiO_3$ perovskite to 9 GPa and 873 K [15]. We have developed a new ultrasonic velocity measurement system that shortens the time for making a P and S velocity measurement from three minutes to one second. This was accomplished by acquiring new equipment (from non-COMPRES funds) that interface to our computer driving systems and then developing software that accomplishes this task. This equipment is open to the scientific public for the first time at the APS BM6B beamline. A similar system will be installed at the NSLS II beamline. We believe that this is not available anywhere else in the world.

Rheology

The quantitative relationship between stress, strain, and time in minerals forms the basis for our view of the evolving Earth. Plate tectonics, earthquakes, volcanic eruptions all respond to these intrinsic properties of Earth materials. Thermal convection in Earth's deep interior cools the planet and in the process generates earthquakes and volcanoes, moves tectonic plates, and disturbs the uniform chemical layering of a differentiated Earth. Laboratory measurements of the relationship between deviatoric stress and deviatoric strain rate of rocks and minerals at high pressure are driven by the need to understand this circulation at depth. Current research on global geodynamics strongly suggests that the dynamics and evolution of this planet are controlled largely by materials properties under deep Earth conditions, including rheological properties, phase relationships, elastic properties and chemical properties such as the diffusivity and solubility of certain elements. For instance, the lateral and radial variation of viscosity have an important influence on the convection pattern and generation of deep earthquakes, whereas the solubility and diffusivity of elements in various phases control the chemical evolution associated with mantle convection. Also, the way in which materials are distributed or the flow pattern in Earth can, in principle, be inferred from seismological observations, but the interpretation of seismological data relies entirely on our understanding of elastic and anelastic properties of minerals under deep Earth conditions. Laboratory studies have recently made a significant breakthrough in capability for defining these properties at mantle pressures and temperatures using x-rays generated by synchrotrons at national laboratories. This progress has set the stage for new and exciting research efforts.

The rheology experiments associated with the NSLS beamline have set an entirely new range of conditions for these measurements. We can now conduct uniaxial stress deformation experiments at 10 GPa and 2000K with near the precision of experiments at 0.3 GPa a decade ago. Through these developments, not only can we infer pressure dependence of mineral properties, but we can examine the properties of high-pressure mineral phases that were impossible before. The technical developments have enabled studies on the relevant properties of minerals [36-73]. We expect to expand this P-T range to 30 GPa and 2500K at the NSLS II beamline.

The new pressure cells and measurement tools also allow a wide array of new characterizations that are still being explored including measurements of phase transition kinetics through stress oscillations with frequencies in the seismic zone[57, 58, 74], Q (inverse attenuation) measurements at high P and T[75-77], thermal diffusivity at high P and T[78-80]. New science will emerge as these tools are used to study polycrystalline samples, partially molten samples, and single-crystal samples. This next five years promises to be a time of great discoveries, taking the tools we have on hand and pushing our understanding of relevant materials.Technical advances

Recent time has seen an ever increasing capability of the experimental program to address significant issues in the Earth sciences. This has come about largely because the user program has included several research groups that have worked with the beamline team to develop many of the new technologies. Some of the advances have come through funding outside of COMPRES such as the 'Grand Challenge' program. Here we summarize some of these advances.

Rheology experimental technique breakthrough

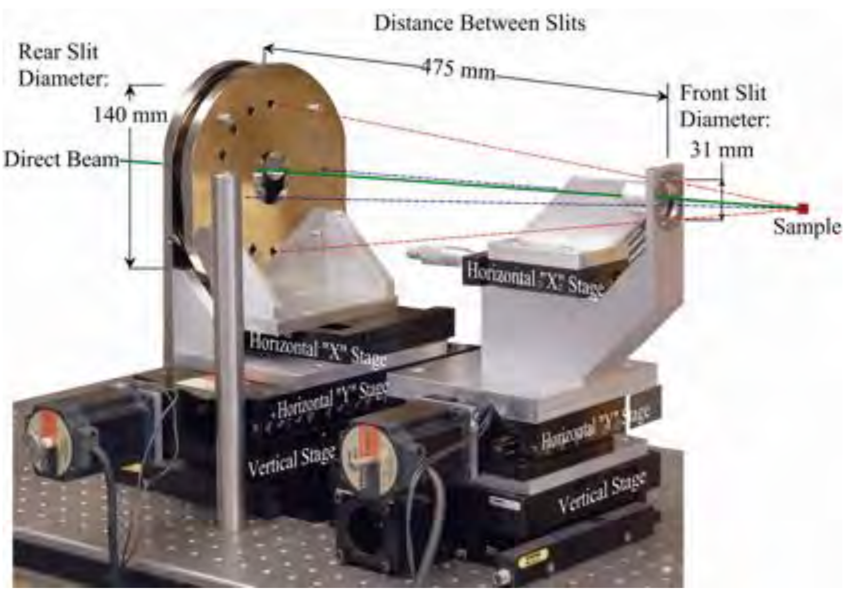
Experimental methods to quantitatively characterize the stress – strain relation in materials at conditions beyond the elastic regime have been limited to pressures of a few hundred MPa. This limits our understanding of the deep Earth not only because we can't simulate the effect of pressure on these properties, but also because we can't study the relevant phases of the deep Earth. In this regard, even pyrope garnet is beyond the reach of these investigations. Over the last decade, the NSLS high pressure program has pioneered the tools that have moved the realm for such studies from the 100's MPa to 10's GPa. The necessary tools for these studies include 1) a compression system that has the capability of adding a well defined deviatoric stress onto the sample, 2) a means for accurately measuring the magnitude of the deviatoric stress, and 3) a means of measuring the strain in the sample. All of these need to be accomplished with the sample at high pressure and temperature and monitored as a function of time.

DDIA

A new high-pressure deformation apparatus, called the Deformation DIA (DDIA), has been married to the synchrotron x-ray source. This new apparatus made its first appearance on a synchrotron beamline at X17 of the NSLS in 2002. In the last decade, its use has matured and it has achieved success beyond the initial hope. Not only has it hosted deformation experiments through its capability of applying a constant uniaxial load to the sample, it has been capable of providing a sinusoidal stress field that has enabled studies of kinetics of phase transition and measurement of Q.

Detector

In situ measurement of stress in polycrystalline samples forms the basis for studies of the mechanical properties of materials with very broad earth science and materials science applications. Synchrotron x rays have been used to define the local elastic strain in these samples, which in turn define stress. We have developed a new, energy dispersive detection system for white radiation, which has been installed at the APS [81]. The new system provides differential strain measurements with a precision of 3×10^{-5} for volumes that are $50\times50\times200$ microns. This gives a stress precision of about 10 MPa for silicate minerals. This system enables accurate steady-state, high pressure and high temperature rheological studies of Earth minerals at mantle conditions.



Conical slit system. Dash-Dot lines represent the diffracted x-rays (red, vertical, blue, horizontal), pointing at the sample. Remotely controlled stages move each slit normal to the direct X-ray beam (green). Slit opening controlled by motion of inner and outer slit components relative to each other.

Sinusoidal stress fields

A new data collection protocol for forced oscillation experiments using a multi-anvil high-pressure device can now be carried out with the DDIA. We derive stress of the sample at high pressure and temperature from synchrotron X-ray diffraction which is synchronized with sample strain measurements from X-ray radiographs. This method yields stress directly from the sample rather than a stress proxy. Furthermore, the diffraction pattern yields useful information concerning time evolution of structurally related phenomena.

The time evolution of a system in a sinusoidal stress field potentially yields a rich array of information ranging from kinetics, anelasticity, lattice preferred orientation induced by grain rotation. X-ray diffraction data are useful for extracting this information at high pressure and temperature. In high pressure dynamic loading experiments [77, 81], stresses are often inferred from the strain of a stress-proxy such as alumina. In this protocol [77], the strain is determined from length changes of the sample and proxy, which are recorded in X-ray images. The data acquisition takes about a millisecond per image. The attenuation can be resolved for periods as short as 10 seconds. This technique has been duplicated at Spring8 for the purpose of measuring Q. A more assumption-free measure of stress comes from X-ray diffraction (XRD) of the sample [72], with the acquisition time close to 500 seconds. However, the beam condition for XRD requires smaller spot size (50µm x 50µm) than X-ray radiograph (2mm x 2mm), and therefore cannot be done simultaneously. We have developed a new strategy of time-synchronization among strain, diffraction-based stress, and applied force-field which enables the experiments when the period is longer than 500 seconds[75]. By using X-ray diffraction and imaging, we are able to examine time resolved elastic strain and total strain, we can compare differential stress derived from the sample with that from a proxy, we can examine changes in lattice preferred orientation *in situ* in an oscillating stress field at high pressure.

Simultaneous Ultrasonic Interferometry and X-radiation Measurements

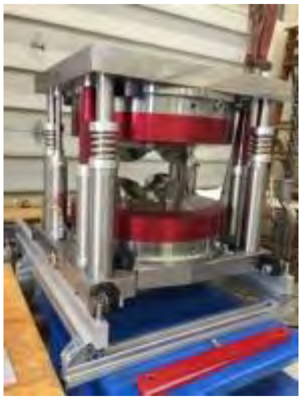
We have developed techniques to conduct simultaneous ultrasonic interferometry, X-ray diffraction and X-ray imaging measurement on solid and liquids at high pressure and high temperature. A series of experiments on minerals relevant to the Earth's deep interior under high-pressure and temperature have been performed and unprecedented data have been obtained. It is worth noting that similar techniques implemented at other synchrotron facilities around the world have all been modeled after the original NSLS set-up. The greatest advantage of the current setup is that a combined analysis of the ultrasonic velocity and X-ray diffraction data on crystalline materials provides a unique means to determine the thermalelasticity with a direct determination of pressure using the sample itself. These techniques can also be applied to (1) reliably determine the density equation of state for glass/amorphous materials through the measurements of ultrasonic velocities with direct sample length measurements (e.g., see data on ZrW_2O_8 [82]), (2) establish absolute pressure scales, and (3) conduct in-situ investigation on time-dependent processes such as phase transformation and melting. Our recent upgrade of the ultrasonic system allows acoustic velocities to measured in 1 second with a system that is interactive with the P-T control system.

Thermal diffusivity at high pressure and temperature

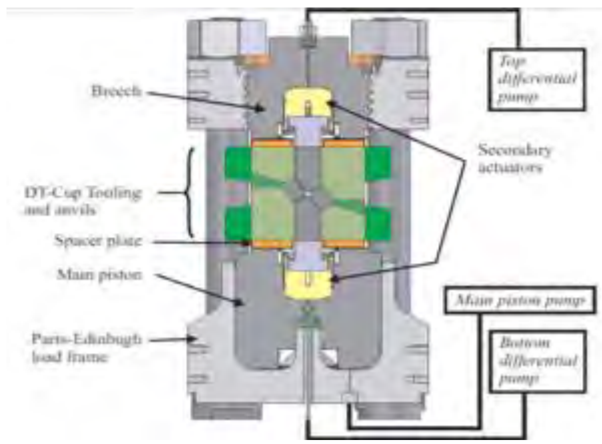
A new method was derived to measure thermal diffusivity of samples at elevated pressure and temperature[78-80]. X- radiograph images of a sample are analyzed to define the distance between two wires as a function of a time varying temperature. The phase lag of the line separation is determined as a function of radius. This phenomena represents the thermal pulse moving into the sample from the furnace. Thermal diffusivity is determined from the motion of the pulse. With this technique, thermal diffusivity is measured for many materials relevant to the Earth's interior.

DT25

The DIA apparatus has x-ray access to the sample that, historically, made it the guideblock of choice for synchrotron experiments. The use of transparent anvils such as sintered diamond removed this restriction and opened up the use of the Kawai style device. The Kawai type device generally can produce at least twice the amount of pressure on a comparable sample as the DIA. We thus focused on designing a



differential stress generation system for the Kawai guideblock with the same philosophy as the DDIA. Together Weidner and Dobson worked with the company that builds the Paris – Edinburgh press to create a DT-10, a cell that fits in their miniature 500 ton press frame that is based on the Kawai compression cell but with additional hydraulic presses that move the upper and lower cubes in the assembly. This provides a differential stress to the system {Hunt, 2014 #83}. The DT10 design is illustrated in the attached Figure. The pistons for the upper and lower rams are located in the main ram and head-piece. The ram itself is an hexagonal post with three truncated corners. This make the post look like one of the cubes from the sample's perspective. This system has been successfully used at the NSLS on a monochromatic beam. We gained a lot of experience with this system and have subsequently built a larger system, a DT25. A picture of the new guideblock is



shown on the right. This guideblock fits into a 1000 ton press. While this system has not yet been tested, we anticipate 30 GPa to be a working pressure range. This system will be installed at the NSLS II beamline.

Time Line

We are now operating the APS beamline. The NSLS II program is currently under construction. We anticipate completion of the installation in a few months. In this budget, the APS program will phase out after one year and all of the experiments will migrate to the NSLS II program, where both a DT25 and a DDIA will be available.

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New Facilities proposed for COMPRES IV

1. Community Extreme Tonnage User Service (CETUS): A 5000 Ton Press Open Research Facility in the United States (PI: Lisa Danielson, Jacobs Technology, NASA Johnson Space Center)

Project Description

Objectives and Expected Significance

Large sample volume 5000 ton multi-anvil presses have contributed to the exploration of deep planetary interiors, synthesis of ultra-hard and other novel materials, and serve as a sample complement to pressure and temperature regimes already attainable by diamond anvil cell experiments (Frost et al., 2004; Liebermann, 2011; Isobe et al., 2013). However, no such facility exists on the Western Hemisphere. We propose the establishment of a Community Extreme Tonnage User Service (CETUS), an open user facility for the entire high pressure research community, with the unique capability of a 5000 ton press, supported by a host of extant co-located experimental and analytical laboratories and research staff.

A large press has a number of potential benefits to expanding high pressure research, as outlined by the COMPRES community at meetings over the past year. The large sample volume in an experiment would reduce sample-capsule boundary interaction effects, but alternatively could be used as a template to study surface interactions at multiple simultaneous interfaces and/or along an imposed thermal gradient. Additionally, a large sample volume at lower mantle conditions would provide opportunities to study minor phases in the mantle, particularly volatile-rich phases. It could also contribute to greater understanding of the thermal conductivity of planetary interiors via experiments with complex mixtures of materials. Another key need identified by COMPRES community members is synthesis of phases at significant quantities to share among researchers and/or for use in multiple applications, a task feasible only with a large volume press. Finally, materials synthesis at high pressure for practical applications requires equipment that produces these materials in a scalable way. Currently, materials characterization for materials at high pressure is severely impeded as many characterization techniques require sample amounts that cannot be produced by standard size multi-anvil presses. For example, the characterization of the pore structure of mesoporous diamond, which require synthesis pressures of 15-21 GPa, could not be quantitatively determined to date because the gas adsorption techniques necessary to determine the pore structure require sample sizes > 100 mg. The limited scalability of materials synthesis available so far, also limits the post-processing and application testing of materials. For example, it would be desirable to synthesize one-dimensional nanostructures of ultra-hard materials by hard-templating techniques, integrate these structures into other materials for their mechanical reinforcement, and then test the mechanical properties of these materials. However, multiple processing steps are extremely difficult if not impossible when only very small quantities of material are available.

Relationship to the Present State of Knowledge in the Field, and Work in Progress by the PI Under Other Support

Relationship to Current NASA Research in Planetary Interiors in Our Division

The large press will benefit experimental studies by allowing experimenters to reach higher pressures (above 30 GPa) and larger sample volumes than is currently achievable with existing presses. Pressures corresponding to the core of Mars and deeper into planetary mantles will be attainable. The large press could also contribute to a greater understanding of physical properties of planetary interiors (e.g., thermal conductivity), rheology, paleomagnetism, all of which are linked by complex early planetary dynamics. This new capability even opens experimental opportunities for studies of the evolution and mantle-core compositions of exoplanets such as super-Earths.

All experimental petrology researchers at NASA JSC investigate element partitioning between major planetary reservoirs, including solid-liquid metal, liquid metal-liquid silicate, solid mineral-liquid silicate, and solid-solid partitioning. Quantifying trace elements in these types of experiments require analytical techniques that can detect ppm to ppb levels of the elements of interest in the various run product phases. Current diamond anvil and high pressure multi-anvil experimentation is limited by size, where the most powerful analytical techniques, LA-ICP-MS and SIMS, cannot be applied to such high pressure experiments because the ion or laser beam areas are typically larger than the experimental samples. This sample size in partitioning experiments is currently limiting, for example, the many groups doing activity coefficient calculations for siderophile elements in metallic liquids because experiments that generate large enough samples can only be done at lower pressure (1 GPa) (Righter et al, 2011; 2016a; 2016b). There is even a problem using a basic technique like EMPA on diamond anvil cell studies, where using thin film corrections can work sometimes on thin FIB sections extracted from the experiment, but not always, and is likely to be a sticking point into the future. With larger sample volumes, there will not be a need to FIB out samples for routine analysis and thus EMPA techniques can be applied to samples without the correction, and for pressure-temperature ranges that might be currently only accessible via DAC (Wade and Wood, 2012). With the large volume multi-anvil press, we will be able to achieve higher pressures with larger samples size, which will enable analyses of samples created at these higher pressures. This could revolutionize our understanding of the detailed partitioning of many elements (siderophile, chalcophile, lithophile) between the major planetary interior reservoirs (Earth, Mars, Venus, super-Earths, exoplanets).

Larger sample volumes will allow better control of the sample environment and complex mixtures of starting materials to be studied in greater detail, expanding the types of conductivity, diffusivity, and phase equilibria studies possible. This larger volume relative to the capsule interior area reduces or eliminates concerns about surface interactions between the sample and capsule, which can swamp experiments at the highest pressures in a capsule of $<1 mm^3$ volume (compare to $1 cm^3$ of a large press at the same pressure conditions). Controlling the oxidation state of the sample by adding solid media buffers would be feasible up to higher pressures. Finally, the potential for studies of volatiles in planetary evolution would be enhanced, with the expanded experimental assembly volume able to contain comparatively sizeable amounts of volatile-rich material within noble metal capsules. This ability opens up more direct simulations of the interiors of the outer planets.

Our Team of Experimentalists and Their Facilities

The Experiments in Extreme Environments Labs (EEELs – includes HPXL, Experimental Impact Laboratory [EIL], 1 bar gas mixing experimental petrology laboratory) are staffed by a vibrant, diverse and growing, close knit research team, composed of 5 civil servant researchers, 6 full time contract research and technical staff, 1 part-time active retired/emeritus staff, 1 visiting scientist from LPI, 1 postdoc, 2 full time on-site graduate students, and 2 graduate student interns.

Team members of EEELs spring 2016, from center-front clockwise: Lisa Danielson[1], PI, HPXL lab manager; Kellye Pando[1]; Loan Le[1]; Roland Montes[1]; Jenny Rapp[1]; Mark Cintala[2]; Dave Draper[2]; Frank Cardenas[1]; Francis McCubbin[2]; Poorna Srinivasan[3]; Kathleen Vander Kaaden[3]; Mya Habermann[1,3]; Kevin Righter[2]; Ian Szumila[1,3]. [1]JETS Contract; [2]NASA civil servant; [3]graduate student. Not shown: John Jones[2], Fred Hörz[1], emeritus; Etienne Medard, visiting scientist, LPI; Asmaa Boujibar, NPP postdoc.

We offer wide range of complementary and/or preparatory experimental options. Any required synthesis of materials or follow up experiments can be carried out in the following: four controlled atmosphere furnaces; two box furnaces, one with a gas retort (to 1000 °C) and one high temperature (1700 °C); 3 piston cylinder presses (3–40 kbar); or the 880 ton multi-anvil press (calibrated to 30 GPa, 2300 °C). Control of fO_2 in high pressure experiments is regularly imposed via addition of buffer material (inside or outside of the sample), or monitored by a sliding sensor (Righter et al., 2013). For experimentalists who need shocked products, we have 3 options: the Light Gas Gun, which can accelerate a projectile to 8 km/sec and has the option of ejecta sample recovery; the Flat Plate Accelerator, which has a cold finger sample holder (down to 77 K) for icy body impact process modeling; the Vertical Gas Gun, with video capture for quantitative modeling of ejecta trajectories. Equation of state experiments are also a development possibility.

Additionally, our division houses two machine shops with technical support staff that would facilitate any modification or custom work necessary for development of CETUS, one for general fabrication and one located specifically within EEELs. Our technical support staff will serve in ongoing maintenance operations of the CETUS facility. We also have a general sample preparation laboratory, specifically for experimental samples, that allows users to quickly and easily prepare samples for ebeam analyses and more.

Analytical Supporting Facilities in Our Division

A service we can offer to COMPRES community members in general, and CETUS visiting users specifically, is a multitude of analytical instrumentation literally steps away from the experimental laboratories. This year we will be pursuing site funding of our laboratories through NASA's Planetary Science Directorate, which should result in substantial cost savings to all visiting users, and supports our mission of interagency cooperation for the enhancement of science for all.

Coordinated analyses of samples is one of the major strengths of our division, where a single sample can be prepared with minimal destruction for a variety of chemical and structural analyses, from macro to nano-scale. The table below outlines the instrumentation available to visitors.

Ebeam Suite Instruments	**Other Microanalyses**	**Additional Laboratories**
FEI-Quanta FIB	ICP-MS	XRD
JEOL 8530F, Cameca SX-100 EPMA	TIMS, GC+Quad MS	Mossbauer
JEOL 7600 FE, 5910 LV SEM	Raman	Nanoscale 3D printer
JEOL 2500 SE, 2000 FX TEM	FTIR	TG, DCS
NanoSIMS	L^2MS (organics)	Soluble organics

A new and exciting opportunity for CETUS visitors is the use of a CT scanner, which will be delivered October 2016 and installed in the same building as all the above mentioned experimental and analytical facilities. This instrument would allow users to construct a three dimensional model of their run product and/or starting material before any destruction of their sample for follow up analyses. This capability would be of particular interest for modeling of differentiation processes, or any experiment with a large compositional contrast in the capsule.

General Plan of Work

The large press configuration will ultimately be guided by the broadest benefit to the research community. Input on the tooling and vendor of choice was gathered at the COMPRES 2016 annual meeting. Additional guidance on science and service objectives, and specific user needs will be gathered at the AGU fall meeting and at a COMPRES/NASA/Lunar and Planetary Institute CETUS working group meeting to be held in January 2017. This working group meeting will also help to define investigator and collaborator roles (see below for more information on current roles) for the project going forward.

There are three phases of work for establishing CETUS, 1) manufacture of the press and components, 2) operational readiness, and 3) ongoing operations. The first item is the responsibility of the vendor (see attached vendor quote). Item two includes lab space renovations, installation, establishing user access and visitation protocols, and experimental cell assembly development. These all are discussed in more detail in sections below, see especially Cost Sharing. Ongoing user work is likely to be funded from a variety of sources, including individual grant awards, COMPRES, NASA facilities funding, and industry partnerships.

The high pressure experimental petrology staff bring decades of experimental knowledge to the CETUS project, and include two members of the ARES management team who can facilitate all aspects of installation of the press and user access and experience. We will work closely with experts in the COMPRES community who can provide additional collaborative efforts on the project.

The HPXL lab manager has planned trips, which are funded by an internal Jacobs outreach travel source, to large press locations worldwide to study operations, meet with press manufacturers, and gain additional experiential insight. This experience will aid in the decisions process of press configuration and development.

We will continue to seek multiple lines of funding during the lifetime of the facility, in order not to rely too heavily on any single revenue stream (see below in Cost Sharing). We anticipate a cost savings during renovation and installation because plans are already underway to renovate HPXL to accommodate our growing user base.

Because CETUS will be an open user facility, we expect outside users to occupy more than 90% of the instrument time. Initially, access will be granted on a semi-formal, as needed basis so that user schedules can be coordinated in order to maximize instrument use time. As demand for service time grows, we will modify access to a more formal proposal system with a mix of internal and external reviewers. We will also welcome proposed experiments that represent innovation, technical development, and pilot studies, in order to promote advances to high pressure studies in planetary sciences. (Also see Cost Sharing section below.)

Users are likely to require varying levels of supervision and support, including the possibility of remote, directed work performed entirely by our expert staff. However, safe operation of this facility will require one of the technical and research staff to be present and assist users at all times, and we will work to ensure this doesn't limit experimental productivity. Our facilities already have procedures in place for working safely after hours.

We are currently developing a user access electronic gateway for our research laboratories, which should facilitate all logistical considerations for accessing CETUS: requesting instrument time; orientation to the lab, ARES JSC, and surroundings; safety training; requests for additional experimental and analytical support, or other instrumentation during the visit; notification of all appropriate ARES personnel; and post-experiment data hosting.

Feedback on operations will be assessed every year during the Lunar and Planetary Science Conference, COMPRES annual meeting, and fall AGU. An online anonymous feedback tool will also be available for visiting users.

Instrument Description
Community input and user needs will ultimately guide the development and final purchase of the large press. Based on preliminary conversations with the future user base, the type of press that would have the greatest utility is a large volume synthesis press. (Also see Voggenreiter quote for more detailed explanation of technical specifications.) The press will be able to hold WC cubes of up to 75 mm edge length. Using adapter plates it will be possible to accommodate WC also smaller cubes down to edge lengths of 25 mm. This way the economics of the experiments will be maximized. A large volume synthesis press scales up the sample volume achievable in a 1000 ton press by a factor of ca. 100, for example, from ~10 mm^3 to ~1cm^3 at 15 GPa. (e. g., Frost et al, 2004).

The figure below (Fig. 1) outlines some alternative pressure generating options for a high tonnage press. Given sufficient interest and demand, it may also be possible to add a separate pressure module for this type of work. Also under consideration would be specific types of pressure generating configurations relevant to deformation studies. All these will be explored concurrently with vendor negotiations during a site visit to the Voggenreiter factory in September 2016 in order to obtain the maximum press functionality for the value.

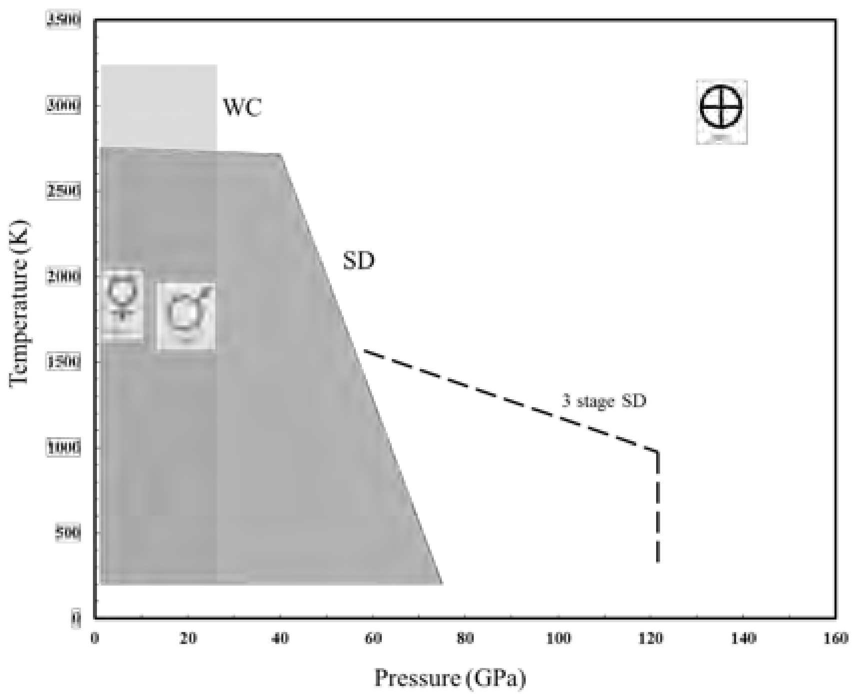

Figure 1. Schematic of achievable pressure-temperature space of multi anvil experiments with various second anvils, modified after Lieberman (2011). Shaded block labeled "WC" (tungsten carbide) is the current pressure temperature regime of multi-anvil apparatuses in the United States. "SD" is sintered diamonds, which require modifications to the pressure module normally used for WC anvils. Even higher pressures have been achieved by use of a 3 stage assembly with additional nano-polycrystalline diamonds, Kunimoto et al. (2008). Symbols for Mercury, Earth, and Mars approximate the core-mantle boundary conditions.

Collaborative Proposal Roles, Managerial Arrangements, and Advantages of the Effort

Investigator Roles
Principal Investigator (PI), Lisa Danielson: direct project as contract lead of HPXL, build user base, engage community support, develop procedures for user access, coordinate

interagency logistics. Collaborator, Kevin Righter: oversee all aspects of project as civil servant lead of HPXL. Collaborator, David Draper: oversee renovations and facility development, develop procedures for user access. Collaborator, Francis McCubbin: contribute to facility development and operational readiness of laboratory. Collaborator, Kurt Leinenweber from Arizona State University: technical development and operational readiness. Collaborator, Kai Landskron, Lehigh University: technical development, build user base and collaborations, contribute to operational readiness. We will also collaborate with Dr. Leinenweber on a separate proposal for development of cell assemblies, modeled after the earlier, highly successful infrastructure and development project "COMPRES Multi-Anvil Cell Assembly Development Project" by Leinenweber, and ASU colleagues Jim Tyburczy, and Thomas Sharp. The new proposal will specifically target the requirements of CETUS, and will reflect community experimental needs expected contribution. Other Professionals, TBD: Two full time technical and research staff will contribute to experimental development, prepare CETUS for operational readiness, maintain the large press, and assist visiting users with experimental and analytical needs.

Our collaborators represent a broad range of petrologists, materials chemists, geochemists, and mineral physicists; they include institutions with which we've had collaborations in the past as well as potential future collaborators and stakeholders interested in utilizing CETUS. Please see letters of support for more information on collaborator interest.

	Corresponding Months	JFM	AMJ	JAS	OND	JFM	AMJ	JAS	OND	JFM	AMJ	JAS	OND
Start Date: January 1, 2017		FY17			FY18				FY20				FY21
		Research Year 1				Research Year 2				Research Year 3			
	Team Members Responsible	Q1	Q2	Q3	Q4	Q1	Q2	Q3	Q4	Q1	Q2	Q3	Q4
Task 1: press order placed													
CETUS Working group	all investigators												
Press manufactured	Danielson, Landskron												
installation	all investigators, new personnel												
lab renovations	Draper, Righter, Danielson												
Task 2: operational readiness													
experimental assembly development	Leinenweber, Danielson, new personnel												
user logistics	Danielson, Draper												
prospective user workshop	all investigators, new personnel												
Attend fall AGU	Danielson												
Attend COMPRES annual meeting	Danielson, Leinenweber, Landskron												
Attend LPSC	all investigators												

Cost Sharing

This facility will be a major undertaking, requiring significant managerial and technical dedication to its success. Because we are devoted to the long term financial health of CETUS by not relying too heavily on any single funding source, and we recognize the model of collaborative success that COMPRES has historically brought to the experimental community, in this proposal we are asking COMPRES and NSF to fund two full time researchers, one early career scientist/technician and one more senior level. These two team members in our research staff will be committed full time in effort to the development and operation of CETUS for the lifetime of the facility. (See attached budgetary forms.) The PI is in a unique position as an employee of Jacobs Technology to draw funding from multiple sources, including those from industry and commerce. On June 3rd, 2016 we submitted a Planetary Major Equipment proposal to the NASA

Emerging Worlds solicitation, requesting the full cost of the 5000 ton press and additional FTE for our project management.

Additional funding is currently being sought from industry sources, which includes materials science researchers; the PI is building a stakeholder base via connections through the Strategic Partnerships Office at NASA JSC, External Pursuits Program Office on the JETS contract, and Jacobs corporate in the United States. We anticipate industry will play a greater role in funding ongoing operations through research and development partnerships, and the PI will be requesting such through Jacobs in the coming weeks. We are also investigating other granting agencies and local funding, such as the Texas Business Development Office, Houston Technology Center, Houston Women's Business Council, Texas Emerging Technology Fund, and many others. Internal funding is available for JETS contract personnel to travel to large press locations worldwide to study set-up and operations. We also anticipate a fortuitous cost savings in installation of the large press because plans are already underway for major renovations to the entire experimental petrology suite within the next 2 years in order to accommodate our growing user base.

Service and Logistical Considerations
We have a strong tradition of collaboration and mentoring. Over the past five years, the 16 full time research and technical staff members in our division have hosted a total of *223 visiting researchers*, representing 35 institutions. Half of these visitors were students, with the remainder a nearly even split between faculty/research staff and postdocs. Because travel and proposed work utilizing CETUS will have a generous lead time, we foresee that we will be able to accommodate the 30 day badging process for foreign national visitors as we have in the past. There are also other options that foreign national experimentalists may wish to utilize: (1) within our division there is already a model for remote work within the Astromaterials Acquisition and Curation Office, where samples can be selected and prepared with the scientist directing the sample preparation remotely; (2) the expert experiment team in our department could handle all work related to the proposed activities if requested; (3) it will be strongly recommended that at least one member of the visiting experiment team be a US citizen. The case of (2) may have additional benefits to users wishing to perform long duration synthesis experiments, but who have travel schedule constraints.

Our focus as contract staff is on serving the scientific needs of our users and collaborators. We will work within a semi-formal, rolling application timeframe in order to best accommodate the experimental requirements of our users and their deadlines. This may necessitate changes over time in order to maximize utilization of the facility while maintaining a fair and open scheduling system, and reflect the evolving nature of experimental demands.

Houston, Texas is an international city and the fourth largest city in the US, with a central location in North America, which would be advantageous to most visitors from this continent. Houston is served by two international airports (Bush Intercontinental and Houston Hobby), each with a dominant international carrier (United and Southwest, respectively). The Clear Lake area, where JSC is located, has many options for affordable lodging, and in general, travel costs to Houston and surroundings are low for a major US city.

Broader Impacts

It is expected that the mineral physics community, materials scientists, as well as those interested in the chemistry of the deep Earth, will make use of the large press, as evidenced by the broad support base and interest in the instrument. A large sample volume at lower mantle conditions would provide opportunities to study planetary scale process relevant to life on Earth, such as minor phases in the mantle, particularly volatile-rich phases, allowing a greater understanding of water and carbon cycling. It could also contribute to greater understanding of the thermal conductivity of planetary interiors via experiments with complex mixtures of materials.

Finally, a key need identified by COMPRES community members is synthesis of phases at significant quantities to share among researchers and/or for use in multiple applications, a task feasible only with a large volume press. Our group's efforts to do this have been limited to low pressures, such as synthesizing Ni- and Co-bearing chromite, MnO and MgO mixtures for starting materials for high pressure studies (Fischer et al., 2014), making V oxides and garnets as beamline X-ray Absorption Near Edge Spectroscopy (XANES) standards (Righter et al., 2006; 2011), and making Fe_3C as a microprobe C standard (Righter et al., 2016). Based on the demand and success even at the narrow, low pressure range, there is huge potential for expanding to higher pressures. The large sample volume in an experiment would reduce sample-capsule boundary interaction, but alternatively could be used as a template to study surface interactions at multiple simultaneous interfaces and/or along an imposed thermal gradient.

The 5000 ton press will greatly facilitate high-pressure materials science because scalability is crucial for comprehensive materials characterization as wells as tool and device fabrication, and testing. The new press will have great utility in synthesizing large quantities of new inorganic, inorganic-organic hybrid, and organic materials in bulk and nanostructured form with potential applications as new ultrahard materials, electronic semi- and superconductors, sensors, and drug deliverers. (e.g., Hazen, 1988).

Larger sample volumes also afford the opportunity to create a library of high pressure samples that can be distributed and shared among any interested researchers. Additionally, we would be able to synthesize high pressure analytical standards that could be shared as well.

Currently, no press of this size exists in North America. Our goal is to serve both the broader high pressure experimentalist and the greater scientific communities with this new technology. We envision an open user facility that is responsive to the changing scientific and technical needs driven by the user base and facility stakeholders. We will set aside operational press time specifically for the purposes of innovation and technical advancement, such as development projects sponsored by COMPRES sub-awards.

The full time user base of the HPXL is currently 67% women, including the PI and two full time technical support staff, a group traditionally underrepresented in STEM fields. We have a strong commitment to engaging and mentoring students, as evidenced by the majority visiting scientist base to ARES. The PI initiated a graduate semester internship program through Jacobs, an activity which increases student participation within our ongoing research. Locating an open user facility such as CETUS within our department will provide additional opportunities to partner with COMPRES' strong tradition of student support and expand our educational and mentoring programs.

Photo from summer 2015, taken for Jacobs Women's Development Network, work role project. L to R: Kellye Pando[1], Mya Habermann[2], Lisa Danielson (PI)[1], Jenny Rapp[2], Carrie MacIntosh[1]. [1]Full time JETS contract research and technical staff, [2]LPI summer undergraduate interns.

Evidence of Research Products and Their Availability

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2. Community Large Multi-Anvil Press Facility (LMAF) at ASU through COMPRES (PI: Kurt Leinenweber, ASU)

We proposed to build a National Multi-Anvil Facility by combining a new 6000-ton press together with existing two 1000-ton presses, two 300-ton presses, and other high-pressure equipment at Arizona State University. The facility will serve the COMPRES community by supporting users in conducting experiments and synthesis of large quantity, high-quality samples at deep mantle pressure-temperature conditions in a large multi-anvil press facility (LMAPF).

Introduction

Figure 1. LMAP at Ehime, Japan

The 6-8 style multi-anvil press has played a vital role in advancing our understanding of processes in the deep interior of Earth and other planets over the past forty-six years since the first report on the technology by Kawai et al. (1970). Over the years, a diverse array of approaches and techniques based on this design have been developed at labs around the world. The standard method uses eight tungsten carbide blocks to press on a ceramic octahedral pressure medium. The size of the blocks was originally 32 mm and the pressure attainable is limited by the deformation or indentation of the steel wedges behind the carbide blocks at the limit of force, or by the size of the press. This configuration can be employed to sample pressures up to about 25 GPa at high temperature (~2000 °C). At these conditions sample sizes are only about 1 mm^3 (a few mg in mass), limiting our capability to study important physical and chemical processes in Earth and planetary interiors.

The pressure barrier and the sample volume limitation have been recently overcome by using larger presses (hereafter referred to as the large multi-anvil press, LMAP) combined with larger carbide cubes (second stage anvils) at Bayreuth and Ehime. The larger carbide cubes are necessary in order not to exceed the yield strength of the steel first-stage anvils that are permanent parts of the press. In the 'Botchan' 6000-ton multi anvil device at Ehime University in Japan (Figure 1), a sample of up to 1 cm^3 can be created at pressures up to 18 GPa and temperatures near 2000 K. In this press, polycrystalline nanodiamonds have been created and then used as anvils to achieve the pressure-temperature conditions of the lower mantle (up to 50 GPa thus far) to study important processes such as element partitioning and the deep transport of water (Irifune et al. 2010; Nishi et al., 2014). At the Bavarian Geoscience Institute (BGI), a 5000-ton press has produced many breakthrough results in Earth sciences, including redox conditions and water and carbon cycles (Frost et al., 2004; Stagno et al., 2013). In the BGI press, bridgmanite samples can be made at 25 GPa with dimensions of up to 3-4 mm diameter (Mosenfelder, pers. comm).

These capabilities are currently lacking in the US. In June 2015, Dan Shim convened a special COMPRES workshop on community needs for a LMAP. Thirty-five scientists came together to discuss the needs and potential of such a system. The results of the workshop indicated community needs and desires for several types of high pressure systems, including the system proposed here. Such capabilities would also have a profound impact on other communities in the US, such as physics, chemistry, materials science, and engineering. This proposal is an outgrowth of that workshop.

Plan for a community-serving facility

We propose to acquire a 6000-ton press to achieve higher pressure-temperature conditions for large volume samples than currently possible in the US. We do not aim to copy the existing capabilities in Ehime and BGI. Our plan is optimized for achieving the broadest possible impacts on the US high pressure community by taking full advantage of ASU's experiences in managing multi-anvil user facilities and developing standardized and special purpose multi-anvil cell assemblies for the community for more than 20 years. The approach we propose is to take advantage of the openness and diversity of the US community to excel in the development of this critical technology for which the US community is at least a decade behind the Japanese and European communities. We propose to have two programs in the facility.

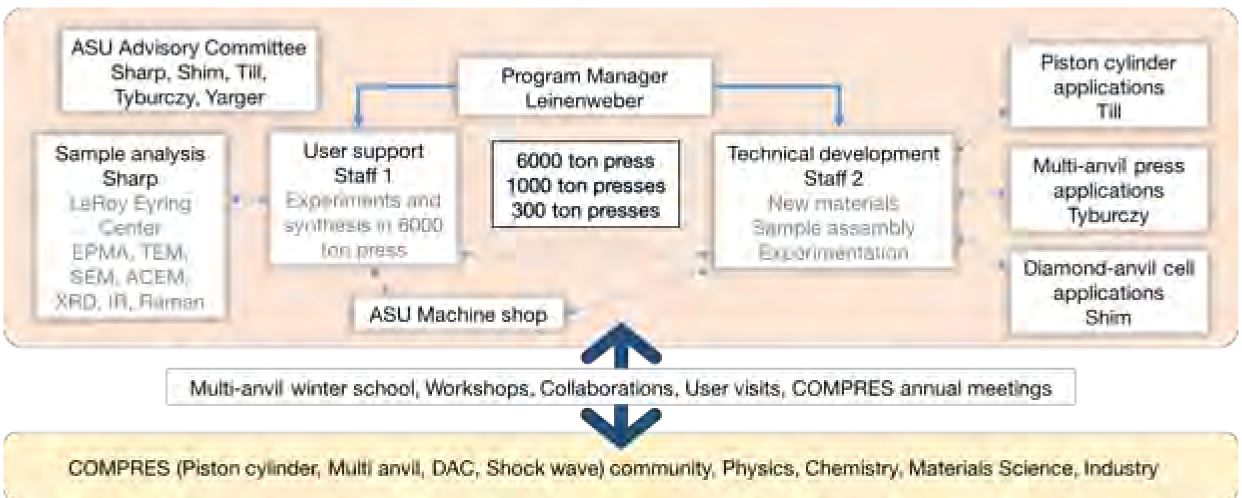

Figure 2. Structure of the proposed ASU multi-anvil press facility and community involvement program.

User program: The large-volume multi-anvil press, LMAP, will be installed alongside currently existing equipment in the ASU high pressure facility consisting of two 1100-ton multi-anvil presses, 3 non-end-loaded piston cylinders, several gas-pressure vessels, a 1-atm gas mixing furnace, 1 atmosphere furnaces, and a laser welder. Sample preparation facilities, saws and other tools also exist in the laboratory. All of these tools will be available to visiting users. A staff member will train and assist the users. The staff will also work with the machine shop at ASU for maintenance of the 6000-ton press and other equipment. We plan to enable users of the facility to conduct the required analysis during their visits, thereby enhancing the success rate of visits. Thus the staff will also coordinate sample analysis with the various analytical instruments available on the ASU campus (EPMA, TEM, SEM, ACEM, XRD, Raman, IR, and FIB, in the LeRoy Eyring Center for Solid State Science, as well as the NMR and NSF-sponsored SIMS and Nano-SIMS facility at ASU) for visiting users.

Development program: The 6000-ton press can make large volumes of high-pressure materials, which opens up the possibility to use these materials as components for high pressure experiments, such as anvils, gaskets, heaters, and electrodes, in the multi-anvil press and diamond-anvil cell. For example, the Ehime group has demonstrated that the LMAP can be used for developing nanocrystalline diamond aggregates that can be used as anvil materials. Also the Misasa group in Japan has developed B-doped diamond synthesized at high pressure in the LMAP, which can be used as effective x-ray translucent heating components for multi-anvil presses and possibly diamond-anvil cells at extreme pressure conditions (Shatskiy et al., 2009). Although such materials have been synthesized using the LMAP in Japan, they have never been openly available to other groups for high-pressure experiments, due mainly to the fact that the programs in Japan are mostly supported by industry and therefore patented (e.g., Sumitomo). By building a community-supported development program at ASU, we will not be bound by such issues and can share new techniques with the whole COMPRES community for the largest possible impact. Such developments will be available for users visiting the facility and will be shared widely with the COMPRES community. This program will also include other experimental technique developments, such as oxygen fugacity control and ultrasound measurements.

We believe that this plan will enable us to achieve the broadest possible impact from a single 6000-ton press, which has not been done by any other LMAPs in other countries. We also believe that our technical developments using the 6000-ton press will enable the COMPRES community to aim for acquiring more specialized LMAPs (large deformation and/or highly aligned multi-axis presses) in other institutions and large user facilities (synchrotron and neutron sources) in the near future.

The plan will also engage the whole COMPRES community in the technical developments through user visits, workshops, and ASU technical experts (Till for PC, Shim for DAC, and Tyburczy for multi anvil press), thereby invigorating research activities in high pressure science that will produce breakthroughs and advance our knowledge in Earth and planetary science, materials physics and chemistry, and engineering. The Center for Solid State Science and SIMS facilities run very successful Winter Schools at ASU every year, and we propose to organize a similar school for high pressure techniques, perhaps coordinating with the other Winter Schools.

Examples for scientific and technical impacts

1. Preparation of large (up to ~1 cm^3) samples of transition zone and lower-mantle minerals for high-quality property measurements, such as deformation, elasticity, calorimetry, diffusion, rheology, and electrical conductivity, etc. We note that some of these measurements have been impossible due to the sample size limitation in the multi-anvil press.
2. Use of large sample assemblies to control oxygen fugacity and other thermodynamic properties of mantle transition zone and lower-mantle minerals and, importantly, complex multi-mineral phase equilibria.
3. In situ experimentation on large samples of mantle minerals – for example ultrasonic and elastic properties (seismic velocity), diffusion, electrical conductivity, rheology,

etc. The ability to perform such measurements is limited by the volume. The device discussed here will facilitate dramatic advances in *in-situ* measurements at high pressures and temperatures.

4. Single crystal growth. Single crystals are uniquely suitable for measurements of any property that depends on direction in the crystal (velocities, structural properties, diffusivities etc).
5. Novel materials to enable higher pressure experimentation. We will pursue experiments that will enable synthesis of polycrystalline nanodiamond for use by the high-pressure community in the US. This material has the potential to greatly expand the pressure range of multi-anvil devices and diamond-anvil cells. This work will also lead to invention and synthesis of other novel materials and has potential for industrial collaborations.
6. Preparation of relatively large volumes of materials to enable sharing of samples between multiple groups for interlaboratory comparisons and calibrations. This work can greatly improve reliability and reproducibility of difficult measurements.

Why ASU?

Since the beginning of COMPRES in 2002, ASU has a long history of community-based development of materials and technologies for multi-anvil cell assemblies. Through the long-term efforts of Leinenweber with advice and assistance from Sharp and Tyburczy, and now others in the Advisory Committee, ASU is extremely well-regarded in its reputation for multi anvil capability combined with community service and communication. The 'COMPRES Multi Anvil Cell Development' project is the longest-running non-beamline project supported by COMPRES. Materials produced by ASU have been (and currently are being) used by scientists all over the world owing to their reliability, reproducibility, and traceable calibrations (see Leinenweber et al., 2012). Till and Shim are now heavy users of the expertise and capabilities of the ASU Multi Anvil facility, and the facility also hosts users from outside Universities on a regular basis. This spirit of supporting the needs of the broader community sets ASU multi-anvil efforts ahead of most facilities. This range of capabilities is also attractive to industrial users who need exploratory high-pressure work, additional expertise, or more accurate pressure-temperature determinations to assist with their industrial processes. The ASU multi-anvil lab already has ongoing research projects with Sandvik Hyperion in Ohio, for example.

ASU also offers a wide array of supporting facilities – those currently in most frequent use for high-pressure research are powder and single-crystal x-ray diffraction, Raman and IR spectroscopy, electron probe microanalysis, NMR, scanning electron microscopy and transmission electron microscopy. However, there are also many other techniques available and users would be able to potentially break new ground with facilities that have not been highly utilized for high-pressure studies (such as SIMS and Nano-SIMS). In addition, there is a state of the art DAC lab (Shim) and end-loaded piston-cylinder lab (Till) that could be accessed through collaboration (these are PI-operated laboratories and not user facilities). Their role is expected to be vital for the development program proposed here as they will be connections for the broader diamond-anvil cell and piston cylinder high pressure communities.

Funding/Budget/Operation Plan

The facility and associated staff will be supervised by Leinenweber in a manner similar to how the current multi-anvil facility is run. We request two staff members for our proposed facility and development program.

We have been accepting outside users into the current high pressure facility at ASU on an open basis – in fact, equal treatment of users is a requirement of the Research Technical Services (RTS) office that supervises ASU facilities. This policy will continue with the renovated facility and the Large-Volume Multi-Anvil Press. Visitors will receive full training in multi-anvil techniques, and advice on sample analysis and help accessing the other facilities at ASU.

Cell assembly materials would be provided to users for the particular experiments they wish to perform. The goal will be to have the full array of cell assemblies for the pressure, temperature and volume ranges needed by the users. What user fees are applied to the experiments, and how to treat COMPRES member users versus other outside users, will be carefully worked out to encourage usage while at the same time allowing the facility to continue operating on a financially stable and sustainable basis.

The development portion of the facility will also be supervised by Leinenweber with input from the local experts (Till for PC, Shim for DAC, and Tyburczy for multi-anvil press). The local ASU experts will also play as liaison to distribute the new technology developed in our program to different high-pressure communities and also to collect feedback from the communities. The COMPRES community and other high-pressure communities will be consulted throughout development including 1) seeking input on the highest priority materials to synthesize, 2) sharing the results of initial development projects and finally 3) in having access to any materials developed through workshops and user trainings.

Budget

The budget for the new facility and the sources of funding are outlined here. The press itself will be sought through an MRI proposal to be submitted through Arizona State University. The cost is expected to be in the range of $3.5M based on a quotation from Sumitomo. This would allow a working press to arrive and be fully installed on the floor of the laboratory. If Sumitomo is selected, it would be necessary to have a hydraulic system manufactured in the United States because the Japanese supplier does not build a system conforming to US standards. A space on ground level, with a solid concrete pad floor and a high bay door to allow the press to be moved in, will have to be created by renovations to an existing space. The cost of renovations is estimated to be $0.75 M and funding would be sought through other channels.

Staff for the facility would require two positions. One senior scientific research staff member would oversee the installation and use of the press; their salary will be requested through COMPRES. A technician would also be needed, and that technician would be funded through other means such as individual NSF proposals.

The budget for materials and supplies is based on the materials needed for large-volume multi-anvil experiments at an anticipated frequency of 100 experiments per year. Large carbide anvils are available from Fujilloy and possibly other manufacturers – sizes such as 52 mm, 65 mm, and 72 mm are available (compared to the "normal" cube sizes of 26 mm or 32 mm used in 1000-ton presses). The Ehime press, for example, is designed to exchange between these sizes depending on need. Prices per cube range from $1000 for the 52 mm cubes to $2000 for the 65 mm ones.

Cube breakage needs to be kept to a minimum, but it can be expected that users will need to go to high tonnages to achieve their research goals. Thus a realistic rate of cube breakage needs to be taken into account. For 100 runs per year, we can expect a breakage of about 100 cubes (estimated one broken cube per experiment). That, combined with the expendables for cell assemblies, leads to the estimated operating costs of $250 K per year (not including personnel). These costs would be sought from COMPRES (for development and testing only), and from the research budgets of grants that are involved in the research goals of each experiment.

Capital

$3,500,000 6000-ton hydraulic press (Sumitomo, Rockland Research, Voggenreiter, etc.) (Will be sought through an MRI proposal).

Laboratory renovations: $750,000 (Will be sought through other sources such as University matching).

Continuing Operations

$309,466/yr Two staff positions – a senior staff position (salary starts at $80,000 per year) and a technical staff position (salary starts at $60,000/year) this includes fringe benefits and indirect costs.

$386,250/yr Operations, including tungsten carbide cubes, ceramics, precious metals (Materials and Supplies) and machining (Facility Use Fees), including indirect costs.

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New EOID projects proposed for COMPRES IV

A Career Path for African-American Students from HBCUs to National Laboratories (PI: Bob Liebermann, Stony Brook)

Summary
The geosciences have the lowest diversity of all the science, technology, engineering and mathematics [STEM] disciplines. To address this poor record, the NSF Directorate for Geosciences established a new program entitled "Opportunities for Enhancing Diversity in the Geosciences [OEDG]." In 2011, we created a new initiative at Stony Brook University: "A Career Path for African-American Students from Historically Black Colleges and Universities [HBCUs] to National Laboratories."

To date, this program has resulted in granting M. S. degrees in Geosciences Instrumentation to 4 African-American students [Ashley Thompson, Adairé Heady, Melissa Sims and Brandon Rhymer] with another student [Brandon Rhymer] to graduate in May 2016; both Melissa Sims and Jesse John are continuing on to the Ph. D. program in The Department of Geosciences at Stony Brook.

This proposal to the Education, Outreach and Infrastructure Development Program of COMPRES is for $180,088 for a two-year period from June 2017 to May 2019 to extend and expand our diversity initiative for another two years. Specifically, we propose to expand our program to include African-American,Hispanic, Native American and disabled students from minority-serving institutions [MSIs], as well as students who are from socio-economically disadvantaged backgrounds. These funds will provide stipends and tuition support for two students to pursue a M. S. in Geosciences Instrumentation. We have requested matching funds from Brookhaven National Laboratory BNL [$50K per year for two years--pending] and the Graduate School at Stony Brook University [$10,870 per year for two years--approved]; these matching funds will enable us to educate an additional graduate student over this two-year period.

Background
The geosciences have the lowest diversity of all the science, technology, engineering and mathematics [STEM] disciplines [Huntoon et al., 2015]. To address this poor record, the NSF Directorate for Geosciences established a new program entitled "Opportunities for

Enhancing Diversity in the Geosciences [OEDG]." In 2011, we created a new initiative at Stony Brook University: "A Career Path for African-American Students from Historically Black Colleges and Universities [HBCUs] to National Laboratories."

A recent report from the American Institute of Physics provides a wealth of data on the presence of African Americans in physics and the geosciences. Entitled "Untapped Talent: The African American Presence in Physics and the Geosciences" [Czujko et al., 2008], it emphasizes that, although "…there are numerous African American students who have adequate high school preparation to succeed in physics, these students are more likely to choose math or sciences other than physics and geoscience in college….Compared to other scientific disciplines, physics and the geosciences consistently come out near the bottom in terms of their ability to attract and retain African Americans." In 2004, the percentages of African Americans earning Bachelor's degrees was 4% for physics and only 2% for the geosciences [compare with 9% for all sciences, which is still below the 13% of African Americans in the U. S. population].

Czujko et al. also examine the educational state of African Americans within the larger context of the U. S. educational system and social structure, including geography and economics. For example, most students go to college near their homes; more than 70% of U. S. universities and colleges awarded no Bachelor's degrees in the geosciences in the five-year period 2000-2004. This situation is even more pronounced at the master's level, despite the fact that more than 500,000 such degrees are awarded each year in the U. S. "The geosciences have the unenviable distinction of having the poorest representation of African Americans (1%) among master's degree recipients." See also the recent report from the NSF: *Women, Minorities, and Persons with Disabilities in Science and Engineering: 2015.*

The goals of this diversity initiative are to: Recruit undergraduate science and engineering students from underrepresented groups that received their undergraduate degrees from minority-serving institutions into the graduate program in the Department of Geosciences at Stony Brook University; Educate these student trainees through formal courses and research projects to the M. S. in Geosciences Instrumentation; Provide these student trainees with a marketable skill set in an emerging field between science and technology; Prepare these student trainees for employment as science associates in national user facilities of the U. S. Department of Energy [DOE], such as the National Synchrotron Light Source [NSLS II] at the Brookhaven National Laboratory [BNL].
The M.S. in Geosciences Instrumentation program includes both formal courses in the Department of Geosciences and internship research conducted at the X-ray beamlines operated at the NSLS and NSLS II of BNL by COMPRES [Consortium for Materials Properties for Research in Earth Sciences]. The internship research projects typically involve the study of the physical and chemical properties of minerals under high-pressure conditions, which is the major theme of the COMPRES consortium, which operates synchrotron beamlines for high-pressure research in the U. S. This new M. S. program addresses well-recognized low levels of participation by minority students in the geosciences and is focused on fostering development and training of the diverse scientific and technical workforce required for 21st century geoscience careers. We are

particularly interested in attracting women in view of the known gender inequality in science, technology, and mathematics, engineering [STEM].
Our program builds on the longstanding relationship between professors from Historical Black Colleges and Universities [HBCUs] and BNL. An outcome of this relationship has been the creation of an Interdisciplinary Consortium for Research and Educational Access in Science and Engineering [INCREASE], an organization whose main role is to support and advance research involving national laboratories and thereby to afford access to research facilities not available to HBCU faculty at their home institutions; our colleague Gabriel Gwanmesia from Delaware State University is a founding member of INCREASE. Over the past five years, we have built a recruiting network including colleagues at INCREASE and other Minority-serving institutions [MSIs] to help us identify and recruit students.

In addition to INCREASE and the National Synchrotron Light Source II of BNL, partners in this new initiative include: the Center for Inclusive Education and the Graduate School of Stony Brook University. All of these organizations have provided matching funds to compliment the NSF funding from Geosciences for the period 2011 to 2016.

This new M. S. program addresses well-recognized low levels of participation by African-American students in the geosciences and is focused on fostering development and training of the diverse scientific and technical workforce required for 21st century geoscience careers. We are particularly interested in attracting women in view of the known gender inequality in science, technology, and mathematics, engineering [STEM] disciplines [e.g., Leslie et al., 2015 and Penner, 2015].

Results from Previous Support
To date, this program has graduated three M. S. students: Ashley Thompson from Delaware State University; Melissa Sims from the University of South Carolina; and Adairé Heady from Delaware State University.

Fig. 1. Melissa Sims, Adairé Heady and Ashley Thompson at X17C beamline at NSLS.

In December 2013, Ashley Thompson successfully defended her MS thesis entitled: “Development of Microreactor System for in situ Invesitgation of Rock-Brine-CO_2 interactions.” In January 2014, Ashley was admitted to the PhD program in Mechanical Engineering at Stony Brook.

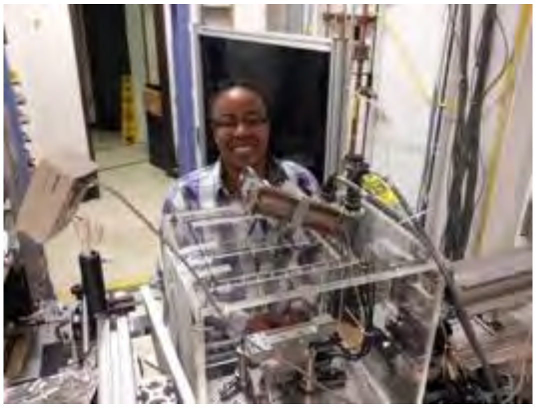

Fig. 2 & 3. Ashley Thompson and Adairé Heady at the X17C beamline of the NSLS at BNL.

In May 2014, Melissa Sims successfully defended her MS thesis entitled: "Beyond FIT2D: Calculating Intensity Errors for Data Analysis of X-ray Synchrotron Powder Diffraction Data." Melissa was admitted to the PhD program in Geosciences in September 2014 and is conducting her thesis research under the supervision of Lars Ehm. In August 2014, Adairé Heady successfully defended her MS thesis entitled: "Internal Resistive Heating of an Almax-Boehler Diamond Anvil Cell", and is seeking employment at a national laboratory such as Brookhaven National Lab.

With graduations of Heady, Sims and Thompson, the first contingent of students in our diversity program successfully achieved their goal of a MS in Geosciences Instrumentation, within a two-year period.

Fig. 4. Commencement day, May 2014. Left to right: Bob Liebermann, Melissa Sims, Ashley Thompson, AdairéHeady, Lars Ehm.

In September 2014, Brandon Rhymer from the University of the US Virgin Islands enrolled in the MS in Geosciences Instrumentation program. Brandon was a summer student at Brookhaven National Laboratory in 2012 and 2013 and was mentored there by Gabriel Gwanmesia and Lars Ehm. Brandon graduated with his M.S. degree in May 2016.

Fig. 5. Brandon Rhymer with 2000 ton uniaxial split sphere apparatus in the Stony Brook High Pressure Laboratory

Melissa Sims, the student mentioned above who is now enrolled in the PhD program in Geosciences and has been awarded a prestigious W. Burghardt Turner Graduate Fellowship by the Center for Inclusive Education and the Graduate School at Stony Brook. Funding from our diversity program will provide the matching and supplemental funding for both Melissa as she proceeds in her doctoral research.

Jesse John from Brooklyn College also holds a Turner Fellowship and is pursuing a PhD in Geosciences under the supervision of Professor John Parise. Funding from our diversity program will provide the matching and supplemental funding for both Jesse and Melissa as they proceed in their doctoral research.

In May 2014, our program “A Career Path for African-American Students from HBCUs to National Laboratories” received the Dean’s Award for Excellence and Innovation in Graduation Education at Stony Brook University. In February 2016, a Project Update on our diversity program was published in the Jul 1, 2016 issue of EOS.

Our program has continued to function fully during the transition from the old NSLS to the newly-constructed NSLSII facility at BNL. In January 2015, during a visit of the State University of new York Research Foundation Board of Directors to NSLSII, a tour of the new X-ray powder diffraction beamline was hosted by Lars Ehm. Melissa Sims gave a short presentation on her thesis project , which involves rapid compression of feldspar minerals and implications for impact cratering processe. Based on her performance on that day and the DOE's interest in cultivating gender and racial diversity in their workforce, Melissa was chosen to introduce Secretary of Energy Ernest Moniz at the dedication of NSLSII in February 2015.

Fig. 6. Melissa Sims from Stony Brook introducing Secretary of Energy Ernest Moniz at the dedication of NSLSII in February 2015 with NSLS Director Steve Dierker at right looking on.

Proposed Research Project

The NSF Directorate for Geosciences has approved a no-cost extension of our grant and both Brookhaven National Laboratory and the Graduate School at Stony Brook have extended their matching funding for another two years to August 2016. Unfortunately, the NSF Directorate for Geosciences has temporarily suspended funding for the OEDG program, so we are seeking new funding from COMPRES to extend the program beyond 2016.

This proposal to the Education, Outreach and Infrastructure Development Program of COMPRES is for $180,088 for a two-year period from June 2017 to May 2019 to extend and expand our diversity initiative for another two years. Specifically, we propose to expand our program to include African-American, Hispanic, Native American and disabled students from minority-serving institutions [MSIs], as well as students who are from socio-economically disadvantaged backgrounds. The attached budget is for $180,088 for a two-year period from June 2017 to May 2019, and includes stipends for the student trainees, travel support to attend annual meetings of COMPRES, tuition and health insurance.
In the attached budget justification, we note that the Research Foundation of the State University of New York has approved budgeting the stipends, travel, tuition costs and health insurance as Participant Support Costs. In this category, these costs do not incur fringe benefits or indirect costs, thereby reducing the budget request substantially.

If funding is approved, we will commence recruiting at MSIs in early 2017. Admitted students can begin their graduate study in Fall 2017, with a combination of formal courses and research projects. Target goal will be to complete their M. S. degree in Geosciences Instrumentation within two calendar years. The PIs will submit Annual Reports to COMPRES describing the progress of this EOID project.

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Infrastructural Development for Deep-Earth Large-Volume Experimentation "DELVE" Yanbin Wang, Tony Yu (GSECARS, APS), Donald Weidner, Matt Whitaker (SBU, NSLS-II), Kurt Leinenweber (ASU), Zhicheng Jing (CWRU), Baosheng Li (SBU), Bin Chen (U Hawaii, Manoa), Yingwei Fei (CIW), Charles Lesher (UC Davis), Shun-ichiro Karato (Yale)

Executive Summary

Deep-earth large-volume experimentation (DELVE) is a two-year proposal requesting funds from the COMPRES Education, Outreach, and Infrastructure Development (EOID)

Program to support development of techniques in multi-anvil presses (MAPs) in COMPRES member laboratories in the US to double the current capability to ~50 GPa. Eleven PIs of nine institutions (with access to both online MAPs at synchrotron beamlines and offline presses in the laboratory) will work together in this initiative, with three major scientific goals in mind, namely, elasticity, petrology, and melt properties under deep earth conditions. We propose to work closely with the Cell Assembly Development Project throughout this effort. The requested funds will be used exclusively for supporting travels of the testing facilities for the development of DELVE techniques for the specific scientific goals. At the end of this project, we project to have near 50 GPa capabilities in all the participating institutions and to deliver a suite of cell assemblies for "ultra-high" pressure experiments to the COMPRES community, along with a few candidate mineral systems for ex-situ high-temperature pressure calibration. We also plan to use the results from this project to jump start larger scientific initiatives such as grand challenge proposals to the NSF aiming at addressing deep earth geophysical problems.

Introduction

In high-pressure research, successful and innovative scientific research relies critically on technological developments. Numerous well-known examples exist. For the diamond-anvil cell , a simple modification (beveling) to the anvils, along with proper gaskets, made it possible to reach multi-megabar pressures (e.g., (Hemley et al., 1997)). Such pressure capabilities, coupled with optical accessibility through the diamond anvils, have made DAC the primary research tool in high pressure physics (Bassett, 2009). However, in characterizing chemical and physical properties of earth materials, stable and homogeneous high temperatures, larger samples (on the order of ~ 0.5 mm), and longer time scales are often required, making multi-anvil press (MAP) an indispensable tool in high-pressure research.

Until the 1960's, the U.S. had been the forerunner in the development of MAP; but Japan gradually took the lead. Today virtually all the MAPs operating in the laboratories worldwide are based on Japanese designs. In the 1990's, the Japanese high-pressure community initiated a ~20 year-long campaign to push the pressure capabilities of the MAPs, breaking the 100 GPa mark in 2014 (Yamazaki et al., 2014), while the development of pressure capabilities in the U.S. has been stagnant for decades and is still limited to ca. 25 GPa today.

Numerous important geophysical problems remain unsolved pertaining to depth range of ~600 to 1500 km, corresponding to pressures between 25 and 50 GPa. Seismic tomography studies have shown that this depth range is one of the most heterogeneous parts of the lower mantle (the other being the large low-shear velocity provinces near the core-mantle boundary). The high velocity anomalies are generally interpreted as subducted slabs penetrating the 660 km seismic discontinuity (Fukao et al., 2009; Fukao et al., 2001). Numerous seismological studies have identified local reflectors in the lower mantle, but their origins are still unclear (Hedlin et al., 1997; Niu et al., 2003; Vinnik et al., 2001). Geodynamical models show that subducting lithosphere penetrates through the upper mantle and the transition zone into the lower mantle (Conrad and Gurnis, 2003; Ricard, 2015), consistent with seismic tomography images. But how do subducted materials interact with the surrounding lower-mantle? How does the interaction affect the mineralogy of the lower mantle, and what is the fate of these materials through geological time? Some lower mantle materials in the up-turning convection flow, on the other hand, may undergo decompression melting at these depths. Petrological and trace element signature of these processes are poorly constrained. A systematic understanding of the petrology of the portion of the lower mantle over a wider composition and temperature range is critical for modeling the evolution of the Earth. Moreover, the advent of space exploration of terrestrial planets and moons also gives rise to tremendous interest in the internal structures of these planetary bodies, particularly the physical states and dynamics of their cores. Pushing the limit of MAPs to 50 GPa would enable investigations of mantle and core dynamics of terrestrial planets and moons, such as Mercury, by covering the whole pressure range of those bodies.

In 2006, COMPRES co-sponsored (along with GSECARS) the development of DDIA-30 at Sector 13 of the APS. After extensive design, construction, and testing, we reported the reach of 35 GPa and 1800 K using sintered diamond (SD) anvils, at the 2010 Fall AGU Meeting (Wang et al., 2010). Subsequent development has been slow due to budgetary constraints. The slow progress may also reflect a dilemma in the collaboration between beamlines and users: Users prefer to use the new technique right away, but the only two existing MAP-based synchrotron facilities in the U.S. lack man-power for the development. In the case of pursuing higher pressures, it is primarily improvement in anvil materials, geometry, and cell assemblies. Knowing that some experiments are bound to fail in the initial phase of the development, it is understandable for general users to shy away as travels to the beamline and conducting test experiments are both expensive and time-consuming. These practical issues plus the fact that SD anvils are inhibitively expensive (about $2,500 each) are the main reasons for the slow progress.

Recently, new tungsten carbide products have become available. The Fujiloy TJS01 carbide (Fig. 1) has been reported to reach 48 GPa using 1.5 mm TEL with tapered cubes and 37 GPa using 3 mm TEL with regular cubes (Kunimoto et al., 2016). This anvil material is made of ultrafine WC powder (~130 nm) with minute amount of Ni binder (≤0.2 wt.%) and small amounts of additives (VC and Cr_3C_2) to suppress grain growth. This new nano-grained WC has extremely high Vickers hardness of 2700 N mm^{-2} and possesses an excellent transverse rupture strength of 2.6 GPa (Wada, 2015). We have contacted the manufacturer (Fuji Dies Co., Ltd) and confirmed the availability of this material as anvils. The price of these anvils is much lower than that of SD. For example, the 14 mm TJS01 anvils were quoted as $350 each. The lower electrical resistance, as compared to that of SD, also makes this new WC more promising to conduct melting experiments at ~50 GPa pressure range.

Here we request funding for a two-year project, in a consorted community effort to double our LPA pressure capability to ~50 GPa. We request funds from COMPRES to support users to GSECARS and NSLS-II beamlines to conduct DELVE experiments, with three scientific goals: elasticity, viscosity, and petrology (more details descriptions of these science projects are given in the next section). We hope that by the end of this two year support, we will obtain some preliminary results on the scientific projects, with several cell assemblies readily tested. These assemblies will then be transferred to the COMPRES Cell Assembly Development Project and made available to the general COMPRES users. The scientific results will be used to jump start an "ultra-high" pressure multi-anvil grand challenge proposal to the NSF.

Three Scientific Goals

Below we identify three major scientific goals to guide this collaborative development project:

1. ***Elasticity of the lower mantle***. The main emphasis is to conduct acoustic velocity measurements on major minerals of the lower mantle, bridgmanite and $CaSiO_3$ perovskite. We plan to employ the ultrasonic techniques to investigate the elasticity of bridgmanite and $CaSiO_3$ perovskite to ~50 GPa and 2000 K. Although elasticity of the pure $MgSiO_3$ endmember is well known, effects of Fe and particularly Al remain controversial. The crystal structure of $CaSiO_3$ perovskite remains controversial under lower mantel conditions (Komabayashi et al., 2007; Kurashina et al., 2004; Ono et al., 2004; Shim et al., 2002) and the effect of Al on its elasticity is still unknown. We plan to investigate the elasticity of Al-bearing $CaSiO_3$ perovskite. Participating PIs: B. Li, Z. Jing, B. Chen, C. Lesher, S. Karato, K. Leinenweber, T. Yu, Y. Wang, and Weidner.
2. ***Melts at high pressure***. Structure and properties of silicate liquids with significant amounts of six-coordinated structural motifs are extremely poorly known. These liquids may have played an important role in the early history of the earth. Understanding liquids in Fe-light-element systems at these pressures are important for constraining composition and structure of planetary cores. Here we plan to develop cell assemblies for studying melting relations, density, and viscosity of silicate and Fe-rich melts up to 50 GPa. Participating PIs: Z. Jing, B. Chen, C. Lesher, S. Karato, K. Leinenweber, T. Yu, Y. Wang, and Weidner.
3. ***Deep earth petrology***. Here we are mainly concerned with interaction between lower mantle mineralogy and subducted lithosphere. For example, the high aluminum content in the slab may affect phase relations in the surrounding mantle, thereby lifting or depressing the local 670 seismic discontinuity. Studies on the stability of dense hydrous magnesium silicates in the subducted lithosphere under lower mantle conditions would provide important information on the cycling of water in Earth. Participating PIs: Y. Fei, B. Li, Z. Jing, S. Karato, K. Leinenweber, T. Yu, Y. Wang, and Weidner.To properly address the above (and many other) scientific problems, synchrotron facilities are a must. Currently, there are very few fix-point calibration materials that can be used for off-line experiments, making off-line development of 50 GPa MAP virtually impossible. Offline development will be pursued after the pressure dependence on load and temperature is established by in-situ work. Once working cell assemblies have been developed, similar assemblies can be quickly adopted in offline laboratories.

Brief Technical Background

To reach ~50 GPa, samples are smaller than the typical size of >1 mm in the MAP. More challenging is to develop cell assemblies that enable us to achieve the scientific goals listed above. The MAPs can be divided into two general configurations. The first and most common configuration is a set of split-sphere or split cylinder first-stage wedges fixed in containment rings, with the eight second-stage cubic anvils (known as the Kawai cell) compressed along the [111] direction of the cube. This configuration may be further divided into two subgroups. The first group has the upper and lower first-stage anvils fixed in two separate containment rings. This configuration provides a horizontal opening for access to thermocouple wires and other probe leads, as well as x-rays. There is no friction between the first-stage wedges and the containment rings under uniaxial load. For in-situ experiments using WC anvils, such geometry is better equipped with energy-dispersive x-ray diffraction (EDXD), to collection diffraction signals through the anvil gaps. The second subgroup is the so-called Walker modules, where all six first-stage wedges are fitted into a single containment ring. During compression, the wedges slide within the containment ring, resulting in additional friction. This type of modules is for ex-situ work only. The second configuration uses a large DIA apparatus to compress the eight second-stage cubic anvils. Compression is along the [100] direction of the cube. Some argue that this configuration has better alignment control, as the movement of the six first-stage anvils can be made precisely in synch. However, this configuration is less load efficient than compression along the [111] direction. X-ray access can be through either the horizontal or the vertical anvil gaps, or both.

A typical cell assembly used in Japan for "ultra-high" pressure generation is shown in Fig. 2. For pressures near 50 GPa, the truncation edge length (TEL) of the cubic anvils are likely around 1.5 to 2 mm. Materials for heaters and sample capsules must be carefully selected, and precision of cell parts is crucial to ensure successful experiments. Various scientific goals impose different constraints on the cell assembly design. For ultrasonic measurements, for example, a buffer rod is needed to connect the sample to the anvil surface for acoustic signal transmission. For melting experiments, possible reaction between the sample and surrounding material must be avoided. Heaters must be able to reach extremely high temperatures (ca. 3000 C). Thermocouple survival rate, which is mainly affected by the tight space and high loads between the anvils, is one of the major challenges in cell assembly development. The main technical goal

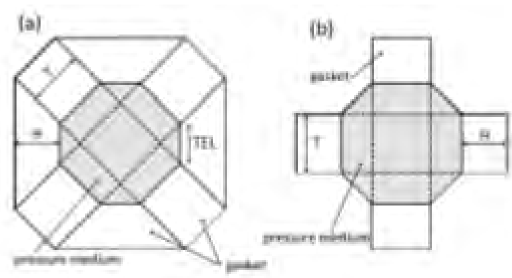

Fig 2 A typical cell assembly for "ultra-high" pressure generation used in Japan. (a) and (b) are top and side views, respectively. Material shaded in grey is octahedron with edges shaved off. It is desirable that the octahedron be made of material with low thermal conductivity. Material in white is gasket. Height (H) and thickness (T) of the gaskets are related to the truncation edge length (TEL) of the cubic anvils. Thermocouple location is not shown.

of this project is to develop a suite of working cell assemblies for both online and offline deep-earth large-volume experimentation (DELVE).

Pressure calibration in off-line laboratories relies on the use of fixed points. There are few such calibrants at pressures above 30 GPa. For our scientific goals, high-temperature calibrations are more important. One of the candidates for high-temperature pressure calibration is the $MgSiO_3$-Al_2O_3 system. Figure 3 shows a phase diagram based on ab initio calculations (Irifune and Tsuchiya, 2007). According their calculations, the alumina content in bridgmanite increases from ~20 mol.% at ~30 GPa to ~40 mol.% at ~50 GPa. This prediction still needs verified experimentally. The solubility of alumina in MgSiO3 perovskite has been used as a pressure calibrant by Hirose and Fei (2002) below 30 GPa, and more recently by Utsumi (personal communication) to a higher pressure with Fujiloy carbide. It will be important to calibrate this and other standards well so that the pressure in offline instruments can be known. As the $MgiO_3$-Al_2O_3 join is an important basis for the understanding of lower mantle equilibria, a systematic study on this system thus can serve dual purposes of this proposed project.

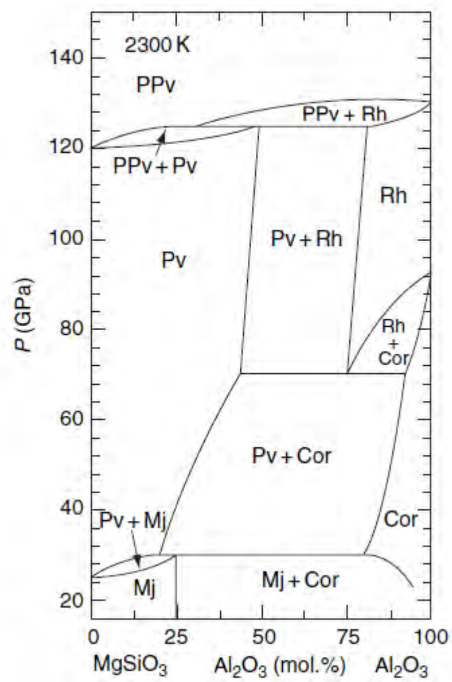

Fig. 3 A calculated phase diagram of the $MgSiO_3$-Al_2O_3 system (Irifune & Tsuchiya, 2007), which can be used for pressure calibrations at high temperatures without x-rays.

Facilities Involved

Each PI has access to at least one MAP in their home institution (Table 1). Many high-pressure modules in the offline labs are essentially the same as T-25 at GSECARS. The one exception is the Stony Brook 2000 ton press, which uses 32 mm cubes. A set of adaptor plates can be used to compensate 26 mm cubes in this system. It is feasible to transfer pressure-load curves calibrated at beamlines to offline labs. Walker modules, which contain all six first-stage wedges in a single containment ring, may have additional friction effects that affect pressure calibration. Such effects can be taken into account by comparing pressure-load curves in different modules using identical cell assemblies.

Online MAP systems are available at both APS and NSLS-II. GSECARS has a 1000 T press operating since 1999 at Beamline 13-ID-D. This station has both white beam and monochromatic beam capabilities. Switching between mono and white beam has been made very easy with the recent modification on the monochromator design. The Si(311) has been routinely used for the DDIA-30 module up to 60 keV. Two multi-anvil modules can be used in the press. The T-25 module has been used extensively for the past 17 years with EDXD. This module compresses eight cubes along the [111] direction of the assembly. This configuration is identical to offline multi-anvil laboratories in the U.S. The 26 mm Fujiloy TJS01 WC cubes are ideal starting point in this module, especially if the cubes need to be tapered to push toward 50 GPa (Kunimoto et al., 2016). Standard COMPRES beamline assemblies have been used in T-25 (Leinenweber et al., 2012). With proper modifications and refinements, these cells can be applied to higher pressures. The cells developed will be transferrable to PIs' offline laboratories as listed in Table 1. The DDIA-30 module has been vigorously tested both in deformation mode and in the double stage mode. Both EDXD and angle-dispersive x-ray diffraction (ADXD) can be conducted in this module. With 14 mm sintered diamond cubes as second stage anvils, pressures up to 35 GPa have been reached at 1800 K, with 1.5 mm TEL at a load of 350 ton (Fig. 4). $LaCrO_3$ and TiB_2 were tested as heater materials. Both worked satisfactorily. The SD anvils were recovered intact after a series of tests to 350 tons, demonstrating the reliability of the system.

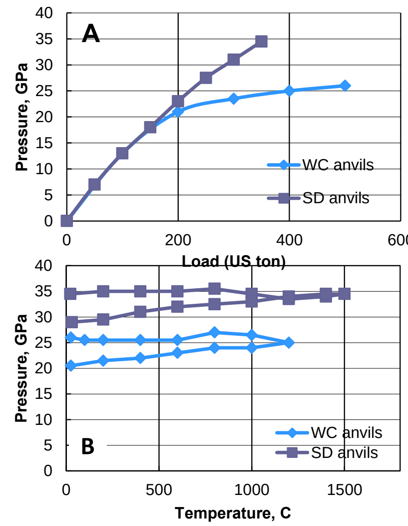

Fig. 4 (A) Pressure generation in DDIA-30 using 14 mm sintered diamond cubs as second-stage anvils (1.5 mm TEL). For comparison, pressure generation using Fujiloy TF05 grade cubes is also shown. Note the steep slope of the curve using SD anvils near 350 T. In comparison, the WC curve has a much shallow slope above 200 T. (B) Temperature generation at high pressure. Both SD and WC anvils show virtually constant pressure during temperature ramp-up. Pressure decreases upon cooling. Cell assembly used was similar to that shown in Fig. 2.

APS provides continuous beam access three times a year, with month-long shutdowns in January, May, and September. Multi-year program proposals are accepted to allow continuous development. All the beam time proposals submitted to APS are reviewed by panel members, with each proposal given a score. Beam time is generally awarded based on the scores. The review panels consist of experts in the respective field outside of the APS. Many COMPRES members have served as members of the review panels in the past. Thus we hope that COMPRES endorsed proposals will be reviewed more favorably. A typical beam time award is 3 to 4 days, which should allow for multiple experiments to test the performance of the cell assembly and collect scientific data.

The new synchrotron at Brookhaven National Lab, NSLS II, is now operational. A multi-anvil 1000 ton press is being installed at the XPD beamline. It is expected to be open for commissioning by the end of the summer, 2016. This press will operate a DT-25 high pressure cell. This cell is similar to the standard T-25 with the addition of independent, uniaxial compression along the axial direction of the press. Thus the system can provide the standard 'hydrostatic' pressure field or one with an additional uniaxial component. There will also be DDIA guideblock that can be interchanged with the DT-25. XPD is a monochromatic beamline optimized to operate at 50 kev, but tunable from 30 to 80 kev. It can be accessed by the standard NSLS II proposal system.

Table 1. MAPs available to the PIs

PI	Location	Capacity (T)	Modules	X-ray accessibility
Wang/Yu	GSECARS, 13-ID-D	1000	T-25[1], DDIA-30[2]	EDXD and ADXD
	GSECARS, 13-BM-D	250	DIA/DDIA	EDXD and ADXD
Weidner	NSLS II XPD	1000	DT-25 [1], DDIA-30[2]	ADXD
	APS 6-BM	250	DIA/DDIA	EDXD
Leinenweber	ASU	1000	Walker [1]	No
		1000	Walker[1]	No
Weidner/Li	Stony Brook	2000	Split-sphere[1]	No
		1000	Walker[1]	No
Karato	Yale	1000	Split-cylinder[1]	No
Lesher	UC Davis	1500	Walker[1]	No
		2000	Walker[1]/Getting Cubic[2]	No
Chen	U Hawaii Manoa	2000	Walker[1]	No
		1000	Walker[1]	No
		250	DIA	No
Fei	Geophysical Lab	1500	Split-cylinder (32 mm) [1]	No
		1500	Split-cylinder (32 mm) [1]	No
		1500	Walker[1]	No
		800	Walker[1]	No
Jing	CWRU	1000?	Walker [1]/DDIA-30[2]	No

Notes: Except for the Walker module and the Getting cubic die, all other modules are "open-jaw" (i.e., two separate containment rings holding the upper and lower guide blocks)

[1] Modules suitable for 25.4 or 26 mm cubic anvils compressed along [111] direction of the Kawai cell.

[2] Modules suitable for 14 and 20 mm cubic anvils compressed along the [100] direction of the Kawai cell.

Another DDIA-30 module, identical to the one at GSECARS, was ordered by Zhicheng Jing from Rockland Research in Oct 2014 and will be installed offline at Jing's high pressure laboratory at Case Western Reserve University. We anticipate installation of this module in the summer of 2016 at CWRU and fully operation of the module by fall of 2017 allowing for a year of setup and fine-tuning time. This system will be used for offline testing of the cell assemblies, after initial test at APS to establish load versus pressure and temperature calibration curves. Such an offline system will add year-round access to the DDIA-30 module complementary to the beamline facility, and hence could significantly accelerate the technical development of cell assemblies. The offline system at CWRU will also be used to study deep Earth petrology and geochemistry and to synthesize lower mantle samples. The system will be made accessible to users in this collaboration during the proposed period of funding and will be open for collaborations with users from the broader high-pressure mineral physics, experimental petrology, and geochemistry communities. Machine time will be assigned based on availability and mutual agreement with Zhicheng Jing. Users in this collaboration who would contribute to the technical development of the cell assemblies and who would need offline tests before beamtimes will be given priority to use the system. An online user registration and scheduling site will be set up to ease the travel arrangements.

In addition, UC Davis has a cubic module designed by Ivan Getting. This module is a single-containment ring module, similar to the Walker module, but compresses six sliding wedges forming a cubic nest, with 20 mm second-stage cubes, similar to that of the DDIA-30.

Work Plan

We will develop experimental protocols and cell assemblies both configurations, in order to help expand pressure capability for the entire community. Major technical development tasks include i) designing working cell assemblies for each of the three scientific goals, optimizing anvil geometry for "ultra-high" pressures, and iii) providing calibrations for the assemblies developed.

Most of the presses we have access to are 1000-2000 ton (Table 1). Tapered anvils, which are more efficient in pressure generation, may be required to reach ~50 GPa. At the same time, sample volume should be maximized, which means anvil TEL should be kept as large as possible. The two geometric parameters for the cell assembly, H, and T (Fig. 1), will be systematically explored to optimize designs of cell assemblies. Additional to these geometric variables are the materials variables. The "octehedra", for example, may be made of ZrO_2, Cr- or Co-doped MgO, or other ceramic materials with low thermal conductivity. $LaCrO_3$, TiB_2, or metals may be used as heaters. Since each scientific goal has different requirements for sample size, temperature capabilities, control of oxygen fugacity, etc., a coordinated, systematic testing approach is the only way to achieve our goals. Testing grids will be established first through group discussion and careful planning. PIs will be divided into three special interest groups (SIG) and be assigned to special tasks to test a given set of parameters.

It is the most critical to develop assemblies for beamlines, as in-situ work will provide pressure-load calibration curves for offline tests. Pressure and temperature capabilities will be tested at synchrotron beamlines. In the initial phase of this development, samples may or may not be directly related to the scientific projects. Once a cell design reaches a stable phase, which is likely to take the first year, parts will be ordered through the COMPRES Cell Assembly Development Project.

Budget Estimate

We are not requesting funds for anvil cost. Both GSECARS and NSLS-II have certain budget for anvil materials used at beamlines. The Multi-Anvil Cell Assembly Development Project has certain budget for anvils, which may be used at ASU and at other participating laboratories with 25.4 mm cube capabilities. The PIs will submit beam time proposals and travel to NSLS-II and APS to conduct in-situ experiments based on the scientific goals. Cell development is a critical part of this collaboration. We request travel support for the PIs to travel to beamlines and CWRU for these experiments. Each trip is budgeted at $1000 (~$400 for airfare and $600 for food and lodging). For the first year, all travels will be to the beamlines so that some proto-type cell assemblies can be established and calibrated. In the second year, some travels to CWRU are requested for offline testing, along with quenched experiments. Table 2 below lists the detailed plan and budget request. For all ten PI's, the total number of trips is 42. Thus we request a funding for two years totaling $42,000 from COMPRES. To simplify accounting activities, the funding may be provided through reimbursement, similar to travel funds for attendees of COMPRES Annual Meetings.

Table 2. Travel plans.

PI	**Year 1**			**Year 2**			**Total trips**
	GSECARS	NSLS-II	CWRU	GSECARS	NSLS-II	CWRU	
Fei	1	1	0	1	1	1	5
Jing	2	0	0	2	0	0	4
Leinenweber	1	1	0	1	1	1	5
Lesher	2	0	0	2	0	0	4
Li	2	0	0	2	0	1	5
Yu/Wang	0	2	1	0	2	1	6
Weidner/Whitaker	2	0	0	2	0	0	4
Chen	1	1	0	1	1	1	5
Karato	1	1	0	1	1	0	4
							42

Result Dissemination

The developed cell assemblies will be published in papers and on the COMPRES Cell Assembly Development Project website. Members of the community can order these parts for them to use. At the end of this project, workshops will be organized to provide hands-on training for those interested in any of the three types of experiments.

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Development of an Electrical Cell in the Multi-Anvil to Study Planetary Deep Interiors (PI: Anne Pommier, UC San Diego)

Project Summary
We propose to design and test a conductivity cell that allows advances in electrical measurements at pressures > 8 GPa using the multi-anvil apparatus. The objective of this project is two-fold: 1) technically, to develop a standardized electrical conductivity cell that can then be widely used at other high-pressure laboratories and 2) scientifically, as part of the testing of the cell, to measure the conductivity of outer core analogues of two terrestrial bodies, Mercury and Mars. Electrical measurements in the laboratory are an excellent probe of the physics and chemistry of melts and minerals. Their use among the high-pressure community has already highlighted that they provide a better understanding of important physical and chemical processes, including the nature of the lithosphere, partial melting at ridges and subduction zones, and the thermal structure of planetary interiors. Our recent work developed a cell that provides high-quality electrical data up to ~8 GPa and we now propose to adapt this cell to work at higher pressure. The application we propose here is to measure the electrical properties of core materials at relevant pressure and temperature conditions to probe the structure and dynamics of Mars and Mercury's core. We are requesting funds for a two-year period to design and test this high-pressure conductivity cell. These measurements are technically very challenging but our reliable and reproducible electrical measurements at lower pressure motivate us to adapt our current electrical setup to pressures up to ~25 GPa. This project will foster collaborations between the high-pressure laboratories at UC San Diego/SIO and ASU, as well as promoting interactions with experimentalists at other high-pressure facilities, geophysicists and geodynamicists. It will also contribute to the training of an undergraduate student and a postdoc researcher at UC San Diego. Developing standardized electrical cells will also provide new technical and scientific directions for the existing MADCAP project (PI: K. Leinenweber) and contribute to promote inter-laboratory communication through the COMPRES community.

Project Description

Objectives and Significance of the Proposed Work
High-pressure conductivity measurements are a topic of timely significance. The augmentation of EarthScope's USArray with a magnetotelluric (MT) array has created an opportunity for development of new interpretive tools to understand MT data in a petrological and geophysical context. A particularly exciting aspect of electrical conductivity measurement under pressure lies in the fact that it is a multi-disciplinary tool. In geophysics, conductivity measurements are used as part of the interpretation of MT anomalies detected in the crust and upper mantle of the Earth (e.g., Pommier, 2014 and ref. therein, Sifré et al., 2014; Pommier et al., 2015a). In materials science, electrical measurements efficiently probe chemical reactions, diffusion processes and melt structure at the atomic scale (e.g., Tyburczy and Fisler, 1995; Pommier et al., 2010). A few studies have also applied electrical measurements to planetary science questions related to the structure of the deep interior of other terrestrial bodies, such as the Moon and Mercury (Deng et al., 2013; Pommier et al., 2015b).

The successful and thus inspiring example of the COMPRES multi-anvil assemblies (Leinenweber et al., 2012) motivates having a standard multi-anvil setup for conductivity measurements designed for inter-laboratory purposes. Few laboratories have developed differing conductivity cells for the multi-anvil (e.g., Dai and Karato, 2009; Yoshino, 2010), suggesting that the quality of electrical data highly depends on the materials selected to build the cell as well as the minimization of noise from furnace and electrodes on the sample's response. The 2-electrode cell we recently developed for the 14/8 (edge length/corner-truncation edge length) assembly has been successfully used to collect high-quality electrical data on silicates up to ~6 GPa (Pommier et al., 2015a,b), but electrical measurements at higher pressure (up to 20 GPa) requires using a 10/5 assembly, and measurements on metals require the use of 3 electrodes.
The community would benefit from reaching consensus about technical challenges, and we propose to achieve it by adapting our electrical cell for the 14/8 assembly to the 10/5 one and standardizing them in order to promote reliable and reproducible measurements through inter-laboratory use. Once developed, these electrical cells would need to be tested and the application we propose consists of investigating the electrical properties of the outer core of Mars and Mercury, whose pressure and temperature conditions can be reproduced in the multi-anvil (Figure 1). Electrical conductivity data of metallic alloys can be used as an alternative approach to constrain thermal conductivity of the outer core (using the Wiedemann-Franz law), as direct measurements of thermal conductivity at planetary interior conditions are technically challenging. The knowledge of thermal conductivity is needed to calculate the heat flux coming from the core, to understand the mechanisms of a dynamo, and to determine the thermal state (e.g., Deng et al., 2013). Thermal conductivity calculations of core materials have provided a large range of estimates, depending on the composition, pressure, temperature and mechanisms (electron-electron and/or electron-phonon scattering) considered. New electrical data on thermal conductivity at core conditions are thus needed to constrain numerical models of planetary evolution. Electrical conductivity data of core materials at conditions relevant to planetary interiors are currently limited and existing studies considered mostly pure metallic iron (e.g., Deng et al., 2013 and references therein).

The primary objectives of this project are:

1. *Technical objective: to develop a conductivity setup for high-quality measurements in the multi-anvil, at pressures relevant for applications to the deep interior of planetary bodies (P up to 25 GPa) (Year 1). The resulting electrical cell will be standardized and made available through COMPRES for a widespread use by the high-pressure community (Year 2).*
2. *Scientific objective: we will test our cells by performing electrical experiments on core analogues (metal alloys) at conditions relevant to the outer core of Mercury (~7-10 GPa), and Mars (~22-24 GPa), in order to study the thermal structure of terrestrial bodies (Years 1 and 2).*

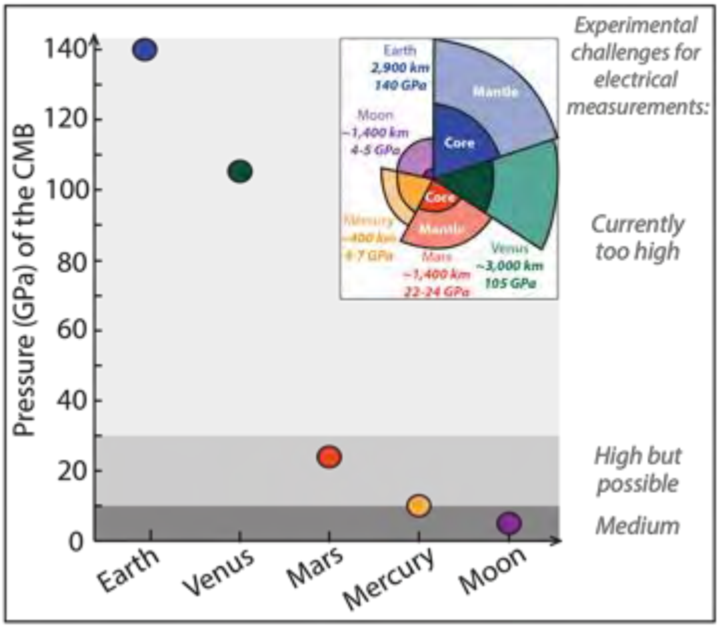

Figure 1: Pressure of the core-mantle boundary (CMB) of terrestrial bodies and related experimental challenges to perform real-time electrical measurements. Currently challenging but achievable pressure for electrical measurements is ~25 GPa, which is relevant to the CMB pressure of the Moon, Mercury, and Mars. Our recent work allows high-quality electrical

Objective 1: Development of a standardized electrical cell

Our current electrical setup designed for the 14/8 assembly is presented in Figure 2 and has been successfully used as part of two recent studies involving partial melting (Pommier et al., 2015a, b). We propose to adapt this cell to the 10/5 assembly and to use a 3-electrode method. Cell design and fabrication of parts will take place at ASU. The electrodes are plugged to a *Solartron* impedance spectrometer and the electrical measurement consists of a scan in frequency (typically from 1MHz to 1Hz). The electrical resistance of the sample R (ohm) corresponds to the real part of the measured complex impedance Z*. The corresponding electrical conductivity ($ohm^{-1}.m^{-1}$ or S/m) is then calculated from the electrical resistance by accounting for the sample geometry. Though these studies present electrical measurements collected at pressure up to 6 GPa (and temperature >2000°C), our cell should allow work up to ~14 GPa. Measurements at higher pressure require the use of the 10/5 assemblies, imposing smaller parts and sample dimensions than for the 14/8 assembly.

Our main challenges and proposed improvements to adapt our 14/8 electrical cell to the 10/5 assembly for measurements on metals can be summarized as follows:

<u>2-electrode vs. 3-electrode measurements</u>: A three-probe method needs to be employed to measure the resistance of metallic samples in order to eliminate the effect of electrodes (their resistance is a few Ohms whereas the sample's resistance will be in the order of micro-Ohms); with a 3-electrode method, resistances measured are due solely to the iron wire itself (e.g., Deng et al., 2013)

<u>Calibration</u>: The contribution of the electrodes to the measured electrical response needs to be negligible compared to the sample's response. To minimize this issue, blank experiments will be performed to carefully quantify on a large T range the influence of the cell on electrical results.

Connection between furnace and electrodes: The small dimensions of the 10/5 assembly parts can cause contact between the furnace and electrodes (which would make a short-circuit). Thus, we will test other electrode configurations and materials (e.g. highly resistive cement) composing the cell to ensure optimal electrodes isolation. Rhenium, TiB_2+BN, boron-doped graphite, lanthanum chromite, and other furnaces will be considered (rhenium being the most frequently used for us at present) furnaces will be considered.

Noise on the electrical measurement: The voltage inside the furnace is a major source of noise on electrical measurements. Optimizing the quality of the electrical response may require the elaboration of a shielding system between the electrodes and the furnace. This has not been necessary for our 14/8 electrical cell, but it may be needed for the 10/5 one. Shortening the length of wires in the press and between the press and the impedance spectrometer is also critical to minimize noise.

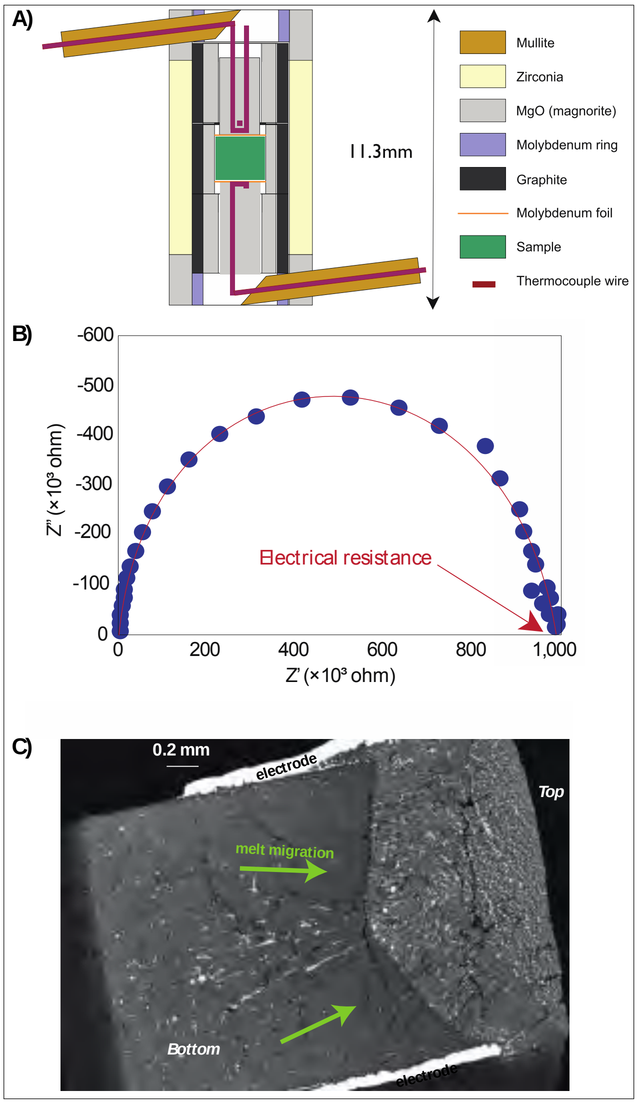

Figure 2: Conductivity setup in the multi-anvil using a 14/8 assembly. A) Cross section of the electrical conductivity cell. With this configuration, the two thermo-couples (TC) also serve as electrodes. Each electrode is made of the TC wires (W-Re), a molybdenum lead and a molybdenum disk that covers the sample's surface. B) Example of a complex impedance spectrum (real part Z' versus imaginary part Z") for a sheared olivine + 5 vol% MORB sample at 750°C and ~3 GPa (Pommier et al., 2015a). The intersection between the response of the sample (each dot corresponding to one frequency) with the Z' axis corresponds to the sample's electrical resistance. The corresponding electrical conductivity value is obtained using the surface of the electrode / sample thickness ratio. C) SEM images of Fo_{77} sample at 6GPa, with visible melt veins and pooling (Pommier et al., 2015b).

Objective 2: Application to planetary outer cores and implications

Electrical experiments using our new 10/5 electrical cell will be conducted at high temperature (~1600-2000°C) and high pressure on synthetic core materials representative of the Mercury core (~7-10 GPa) and Mars' outer core (~22-24 GPa). Analog core compositions will consist of iron + nickel for the two terrestrial bodies, and variable amounts of sulfur (from ~5 to 15 wt% S) will be added.

Experiments will be performed in the multi-anvil apparatus at the new UC San Diego – Planetary and Experimental Petrology Laboratory (PEPL) using the three-electrode method. Materials that make the conductivity cell will be chosen in order to minimize chemical interactions with the sample. The conductivity cell will be connected to a 1260 Solartron Impedance/Gain-Phase Analyzer for electrical impedance measurements over the frequency range 5 MHz-0.1Hz. Redox conditions (oxygen fugacity) are an important factor in the evolution of planetary interiors as they control the composition of magmas and volatiles derived from a source reservoir. The redox conditions defined for Mars and Mercury being reduced, around or below the Iron-Wüstite (IW) buffer (e.g., Wadwha, 2008) iron electrodes will be used for most runs in order to help buffer the sample at redox conditions close to IW. Changes in electrical resistance will be recorded until a constant value is reached, underlining electrical equilibrium. Samples will then be quenched and retrieved for chemical analyses at ASU.

Based on these electrical measurements, corresponding thermal conductivity and heat flux will be calculated for Mercurian and Martian outer cores. Our laboratory-based values will be compared with heat flux estimates from numerical models (e.g., Williams and Nimmo, 2004; Tosi et al., 2013) to help constrain existing thermal models. Our results will also be compared with the heat flux determined from electrical experiments on iron by Deng et al. (2013). The latter study estimated a heat flux in the outmost core of Mercury and Mars of 0.29-0.36 TW and ~6 TW, respectively. A low heat flux for Mercury is consistent with its weak intrinsic magnetic field and the hypothesis of a self-sustained dynamo. The larger Martian heat flux suggests that heat loss from the core is a significant contribution to the total heat loss at the surface of the planet. The outcomes of our project will help understand the time-evolution of magnetic field stability and dynamics at the scale of a planet and are thus critical to future numerical models of core-crystallization regime and planetary-scale convection (Davies and Pommier, in review). Our results will also be relevant to larger terrestrial planets, such as the Earth.

Broader Impacts

We propose to standardize our conductivity cell for multi-anvil experiments in order to make it available to the high-pressure community. This project will strengthen collaborations between the ASU and PEPL laboratories. Such an initiative of standardization for inter-laboratory use can only be achieved if scientific knowledge is shared among different laboratories. We will thus interact with laboratories that perform electrical studies in the US and other countries (Japan, France, Germany) during the development of the electrical cell, in order to share our outcomes and benefit from their experience. A widespread use of our setup will promote multi-disciplinary investigations, in particular with geophysicists and planetary scientists. The electrical data we propose to collect on core analogues will also be of high interest to the geodynamical community, as these data will provide new estimates of thermal conductivity and heat flux in planetary interiors that are requested as part of thermodynamic modeling.

This project will be overseen primarily by Anne Pommier and will help continue the training of undergrad student Jennifer Maria Benavides as an experimentalist and of postdoc Johnny Zhang at UC San Diego-SIO to perform electrical measurements under pressure. It involves new initiatives outside of the COMPRES Multi-Anvil Cell Assembly Development project led by Kurt Leinenweber (MADCAP). The development of expertise in electrical measurements is an initiative that is not envisioned in the other project. The key element is the active testing and use of cells at UC San Diego that will feed back into the cell designs.

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