**Beamline scientist annual report for the year of 2016**

**Name:** Dongzhou Zhang

**Position:** Partnership for extreme crystallography beamline scientist (APS 13-BM-C)

**Length of time at current position:** one year and ten months, since January 2015.

**Brief job description:** The PX^2 program is a collaboration between the University of Hawaii and the GeoSoilEnviroCARS beamline at the APS, and is fully supported by COMPRES. My job is to design, build, and maintain the state of the art instrumentation for the PX^2 project at Argonne National laboratory, and support user program in high-pressure science at the PX^2 facility.

**Activities:**

My activities in the year of 2016 are majorly divided into two categories: beamline development and user support. In each run cycle (~12 weeks of beamtime + ~4 weeks of shutdown time), approximately 6 weeks of beamtime are used for non-high-pressure surface diffraction experiments, with the remaining 6 weeks available for COMPRES diamond anvil cell (DAC) users. PX^2 is still in a phase of active commissioning (new online ruby-Raman spectroscopy table has just been installed in the summer of 2016), and we have been using about 1 week, out of the available 6 weeks of DAC beamtime for commissioning activities. Commissioning, and instrument development and improvement activities that do not require X-ray beam are also carried out during shutdown periods.

*Beamline development*

- Compact optical platform for ruby pressure determination and Raman spectroscopy: Pressure determination is important for diamond anvil cell experiments. Currently, the most convenient method to determine the pressure in the sample chamber is ruby fluorescence. I installed a compact optical platform to the 13-BM-C station in early 2016, which is capable of determining pressure with ruby fluorescence, as well as collecting Raman spectra on the sample. This compact optical platform has been appreciated by the users. With this platform, the users can easily control the pressure of their diamond anvil cells with membrane pressure controller.

- Resistive heating and temperature readout setup: 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. I upgraded the remotely-controllable resistive-heating and temperature reading setup in the experimental station 13-BM-C. With the support from COMPRES, a new 1000-W power supply has been purchased to power the heaters in the DACs, and a new thermal couple reader has been installed, which provides a faster temperature readout rate and requires less computational resource than the old Keithley-type digital multimeter. The setup is capable of heating the samples up to 1000 C, and has been used by the users since the run of 2016-2.

- Membrane pressure controller update: Diamond anvil cells mounted in membrane pressure controller allows pressure to be changed remotely, and is therefore more convenient for user operations. In early 2016, I installed the membrane pressure controller in 13-BM-C, with automatic remote control capability. This setup significantly reduces the time needed for the users to change the pressure of their sample, and is appreciated by the users. The membrane pressure controller is working synergistically with the resistive-heating setup and the compact optical table. In one of our test, the users can control the data collection process remotely from the University of Hawaii’s campus in Honolulu.

- X-ray instrumentation: In diamond anvil cell experiments, most of the experimenters use X-ray pin-diode to scan and align the sample’s position. In the past, the X-ray pin-diode in 13-BM-C was bulky, pneumatically-driven, moving in-and-out during the measurement, which caused significant instability to the other components. I replaced the old X-ray pin-diode with a new compact pin-diode incorporated into the X-ray beamstop. This integrated pin-diode beamstop provides additional stability to the diffractometer.

- Software development: In the mid-2016, with the help of Dr. Jesse Smith from HPCAT, I updated the single crystal diffraction data collection software in 13-BM-C. This new software is based on Python, rather than the old IDL 6.4 program, and it provides a better time synchronization between the X-ray shutter and the X-ray detector.

*User support and scientific research*

In the past year, I supported more than 20 groups of users from COMPRES member institutions. Both single crystal diffraction and powder diffraction data were collected, and the pressure-temperature range covers 0-100 GPa and 25-1000 °C. In the past year, we had 3 manuscripts published in peer-reviewed journals, and several more are currently under review. The following paragraphs demonstrate select user publications that are related to experiments carried out at PX^2.

- Synthesis of FeO2 and the Fe-O-H system in the deep Earth (Hu et al., **Nature**, 531, 241-244 (2016), highlighted by COMPRES website). 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 O2 and heated above 76 GPa and 1800 K, a new FeO2 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 FeO2 diffraction pattern was solved by the so-called multigrain crystallographic method. The newly discovered FeO2 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 FeO2 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, FeO2 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.

- Band-gap narrowing together with carrier-lifetime prolongation in perovskite-structured compound (Kong et al., **PNAS**, 113 (32), 8910-8915 (2016)). Hybrid organic-inorganic perovskites are believed to be one of the most promising materials the next generation of solar cells. The solar cells convert solar energy into electrical energy so it's a sustainable and environmentally friendly energy source, giving high performance at a low cost. In addition to solar cell technologies, the hybrid perovskites have potential to be used in a variety of optoelectronic applications. Its power-conversion efficiency has been increased to 22.1% at present. High absorption for solar energy and photovoltage for longing the carrier-lifetime in hybrid perovskites are key factors for their actual usage in energy science.

- Compressional behavior of omphacite (Zhang et al., **PCM**, 43(10), 1-9 (2016)). Omphacite is an important mineral component of eclogite. Single crystal synchrotron X-ray diffraction data on natural (Ca,Na)(Mg,Fe,Al)Si2O6 omphacite have been collected at the Advanced Photon Source 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 V0=423.9(3) Å3, KT0=116(2) GPa and KT0’=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 SiO4 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.

*Crystallographic Training*

- User training in data collection during experiments: I work extensively with Prof. P. Dera from the University of Hawaii at Manoa in learning and developing single crystal diffraction data collection software and crystallographic computational tools. I wrote the manual of basic operations in the PX^2 beamline for high pressure DAC users, and the manual of data collection software. I trained all the first-time users to collect data properly at our beamline.

- User training in data analysis and post-experiment user data evaluation: PX^2 is a brand new instrument for DAC studies and since it is very different from typical high pressure DAC installations, majority of users who come to PX^2 for the first time require extensive training in the data collection procedures and data analysis process. Very often my help in the data evaluation continues long after the experiment is over, particularly in cases when data shows interesting phenomena or is of lower quality (e.g. twinning, crystal breakage after phase transition, etc.)

*Outreach and Conference presentations*

- I was invited to give a talk at the 2015 AGU Fall Meeting in San Francisco, California. I presented a poster about the development of the PX^2 program. During this conference, I attended the COMPRES townhall meeting and gave a talk about the future development of PX^2. I also received the 2015 MRP Graduate Research Award.

- In January 2016, I visited the HPSTAR Beijing center in Beijing, China, and gave a talk about the development of the PX^2 program. HPSTAR is one of the biggest high pressure research centers in Asia. Several people in my audience later became visiting scholars to COMPRES member institutions, including the Geophysical Lab and Florida International University, and they applied beamtime in PX^2.

-In May 2016, I attended the APS user meeting in Argonne, Illinois. I gave a poster about the development of the PX^2 program.

- In June 2016, I attended the COMPRES Annual Meeting in Tamaya, New Mexico. I was invited to give a talk about the development of PX^2 program. In addition, I gave a poster to show the progress of the beamline development.

- In June 2016, I attended the 49th International School of Crystallography in Erice, Italy. I presented a poster about the development of the PX^2 program. Several attendees of this summer school, including researchers from the University of Utah and Stanford University, later applied for beamtime at the PX^2.

- In October 2016, I attended the high pressure multigrain diffraction workshop organized by HPCAT. I presented a talk about the experimental capabilities at the PX^2.