**Beamline scientist annual report for the year of 2018**

**Name:** Dongzhou Zhang

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

**Length of time at current position:** three years and eleven 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 2018 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 3 weeks of beamtime are used for non-high-pressure surface diffraction experiments, with the remaining 9 weeks available for COMPRES diamond anvil cell (DAC) users. PX^2 is still in a phase of active commissioning (new time-resolved Pilatus detector has just been commissioned in the summer of 2018), and we have been using about 1 week, out of the available 9 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*

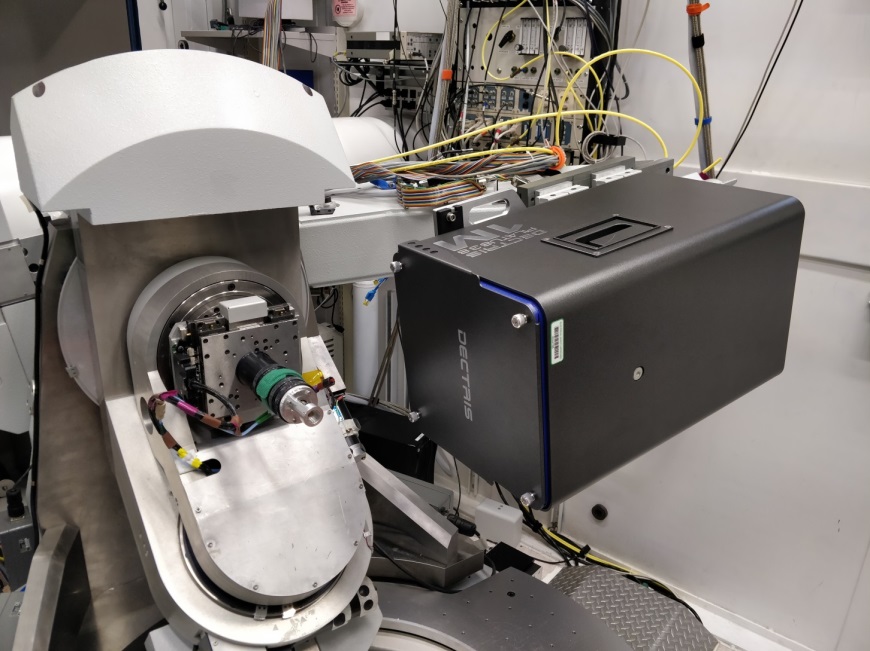
- Time-resolved Pilatus 1M detector: After 2 years of operation, PX^2 started to see a beamtime oversubscription in early 2017. To meet the increasing beamtime request, we decide to replace the 15-year old and slow MAR165 CCD to a state-of-the-art time-resolved detector. COMPRES agreed to fund the detector in mid-2017. Between 2017 and 2018, several detectors were tested at PX^2 with the help of GSECARS staffs, including Pilatus, Bruker Photon II, Perkin Elmer and Dexela. After careful tests on the detectors, we decided to purchase Pilatus3S 1M detector with 1 mm Si in May 2018, because of its fast-readout rate, low background, good quantum efficiency and large dynamic range. COMPRES and GSECARS co-funded the detector. The Pilatus3S detector arrived in August 2018, and was commissioned in October. User operation with the Pilatus 1M detector will start in the Run 2019-1.

Figure 1: The new Pilatus 1M detector mounted on the diffractometer at 13-BM-C during the 2018 October commissioning.

*User support and scientific research*

In the past year, I supported more than 50 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 25-800 °C. In the past year, we had 18 manuscripts published in peer-reviewed journals, and several more are currently in press. The following paragraphs demonstrate select publications that are related to experiments carried out at PX^2, and I am co-author on all of the following papers.

- **Valence and spin states of iron are invisible in Earth’s lower mantle (Liu et al., Nature Comm. 2018, 9:1284).** Heterogeneity in Earth’s mantle is a record of chemical and dynamic processes over Earth’s history. The geophysical signatures of heterogeneity can only be interpreted with quantitative constraints on effects of major elements such as iron on physical properties including density, compressibility, and electrical conductivity. However, deconvolution of the effects of multiple valence and spin states of iron in bridgmanite (Bdg), the most abundant mineral in the lower mantle, has been challenging. Here we show through a study of a ferric-iron-only (Mg0.46Fe3+0.53)(Si0.49Fe3+0.51)O3 Bdg that Fe3+ in the octahedral site undergoes a spin transition between 43 and 53 GPa at 300 K. The resolved effects of the spin transition on density, bulk sound velocity, and electrical conductivity are smaller than previous estimations, consistent with the smooth depth profiles from geophysical observations. For likely mantle compositions, the valence state of iron has minor effects on density and sound velocities relative to major cation composition.

- **Phase Transitions in Orthoenstatite and Subduction Zone Dynamics: Effects of Water and Transition Metal Ions (Xu et al., JGR-Solid Earth, 2018, 123:2723-2737)**: Synchrotron-based high-pressure and temperature single-crystal X-ray diffraction experiments were conducted on two hydrous orthoenstatite samples (oEn#1: Mg1.004Si0.996O3, ~619 ppm water; oEn#2: Mg0.947Ni0.055Si0.998O3, ~696 ppm water) to ~34 GPa and 700 K, using resistively heated diamond anvil cells. The α-opx (Pbca space group)→β-opx (P21/c space group) phase transition of oEn#1 occurs at 12.90(2) GPa, and the β-opx phase persists to 34.25(1) GPa. The α-β transition of oEn#2 occurs at 13.50(1) GPa, and a new isosymmetric β-opx→β-opxII transition takes place at 29.80(4) GPa. The β-opxII phase is preserved down to 24.53(3) GPa during decompression. The transition to the monoclinic β-opxII phase is interpreted as a result of incorporation of Ni2+ into the orthoenstatite structure. Fitting the third-order Birch-Murnaghan thermal equation of state to the single-crystal P-V-T data yields the thermoelastic parameters of the α- and β-opx phases for both orthoenstatite samples. This study is the first attempt to determine the thermal equation of state of the β-opx phase. Our results suggest that several hundred ppm of water has negligible effects on the bulk modulus of orthoenstatite but notably enhances the thermal expansion. The potential effects of metastable orthoenstatite on subduction zone dynamics are discussed, and the possible contributions of displacive phase transitions to enhancement of the transformational faulting mechanism of the deep-focus earthquakes in subducted slabs are considered. The presence of metastable orthoenstatite within cold slabs could promote slab stagnation above the 660-km discontinuity.

- **The high-pressure anisotropic thermoelastic properties of a potential inner core carbon-bearing phase, Fe7C3, by single-crystal X-ray diffraction (Lai et al., American Mineralogist, 2018, 103:1568-1574).** Carbon has been suggested as one of the light elements existing in the Earth’s core. Under core conditions, iron carbide Fe7C3 is likely the first phase to solidify from a Fe-C melt and has thus been considered a potential component of the inner core. The crystal structure of Fe7C3, however, is still under debate, and its thermoelastic properties are not well constrained at high pressures. In this study, we performed synchrotron-based single-crystal X‑ray diffraction experiment using an externally heated diamond-anvil cell to determine the crystal structure and thermoelastic properties of Fe7C3 up to 80 GPa and 800 K. Our diffraction data indicate that Fe7C3 adopts an orthorhombic structure under experimentally investigated conditions. The pressure-volume-temperature data for Fe7C3 were fitted by the high-temperature Birch-Murnaghan equation of state, yielding ambient-pressure unit-cell volume V0 = 745.2(2) Å3, bulk modulus K0 = 167(4) GPa, its first pressure derivative K0ʹ = 5.0(2), dK/dT = –0.02(1) GPa/K, and thermal expansion relation aT = 4.7(9) × 10-5 + 3(5) × 10-8 × (T – 300) K-1. We also observed anisotropic elastic responses to changes in pressure and temperature along the different crystallographic directions. Fe7C3 has strong anisotropic compressibilities with the linear moduli Ma > Mc > Mb from zero pressure to core pressures at 300 K, rendering the b axis the most compressible upon compression. The thermal expansion of c3 is approximately four times larger than that of a3 and b3 at 600 and 700 K, implying that the high temperature may significantly influence the elastic anisotropy of Fe7C3. Therefore, the effect of high temperature needs to be considered when using Fe7C3 to explain the anisotropy of the Earth’s inner core.

**- Suppression of the magnetic order in CeFeAsO: Nonequivalence of hydrostatic and in-plane chemical pressure (Materne et al., PRB, 2018, 98:014517).** We present a detailed investigation of the electronic properties of CeFeAsO under in-plane chemical (As by P substitution) and hydrostatic pressure by means of in-house and synchrotron Mössbauer spectroscopy. The Fe magnetism is suppressed due to both pressures and no magnetic order was observed above a P-substitution level of 40% or 5.2 GPa hydrostatic pressure. We compared both pressures and found that the isovalent As by P substitution changes the crystallographic and electronic properties differently than hydrostatic pressure. This work is a collaboration between PX^2 and APS Sector 3-ID, which is partially supported by COMPRES as well.

**- Equations of State and Anisotropy of Fe-Ni-Si Alloys (Morrison et al., JGR-Solid Earth, 2018, 123:4647).** We present powder X-ray diffraction data on body centered cubic (bcc)- and hexagonal close packed (hcp)-structured Fe0.91Ni0.09 and Fe0.8Ni0.1Si0.1 at 300 K up to 167 and 175 GPa, respectively. The alloys were loaded with tungsten powder as a pressure calibrant and helium as a pressure transmitting medium into diamond anvil cells, and their equations of state and axial ratios were measured with high statistical quality. These equations of state are combined with thermal parameters from previous reports to improve the extrapolation of the density, adiabatic bulk modulus, and bulk sound speed to the pressures and temperatures of Earth’s inner core. We propagate uncertainties and place constraints on the composition of Earth’s inner core by combining these results with available data on light-element alloys of iron and seismic observations. For example, the addition of 4.3 to 5.3 wt% silicon to Fe0.95Ni0.05 alone can explain geophysical observations of the inner core boundary, as can up to 7.5 wt% sulfur with negligible amounts of silicon and oxygen. Our findings favor an inner core with less than ∼2 wt% oxygen and less than 1 wt% carbon, although uncertainties in electronic and anharmonic contributions to the equations of state may shift these values. The compositional space widens toward the center of the Earth, considering inner core seismic gradients. We demonstrate that hcp-Fe0.91Ni0.09 and hcp-Fe0.8Ni0.1Si0.1 have measurably greater c∕a axial ratios than those of hcp-Fe over the measured pressure range. We further investigate the relationship between the axial ratios, their pressure derivatives, and elastic anisotropy of hcp-structured materials

*Outreach, Crystallographic Training and Conference presentations*

- IUCr HP workshop 2018: Between July 29 and August 2, the International Union of Crystallography (IUCr) high pressure commission held its annual workshop in Honolulu, HI. The theme of the workshop is “Extreme materials, extreme phenomena, extreme environments”. I participated in the workshop as a member of the organizing committee. The workshop is partially supported by NSF through funding EAR-1834441, and I am the co-PI of this funding. COMPRES supported a satellite hands-on training session for students and junior scholars in the day prior to the workshop, and I gave a lecture in the training session to teach the young scientists about the basics of high pressure crystallography experiment. The workshop was well received. More than 120 researchers from North and South America, Europe, Asia and Oceania attended the workshop, and 83 oral and poster presentations were made in the workshop.

- In 2018 I attended the following conferences and gave presentations: APS/CNM annual meeting (Argonne, IL, May 2018); COMPRES annual meeting (Albuquerque, NM, August 2018). I am going to attend the 2018 AGU Fall Meeting (Washington, DC, December 2018). I am a convener of the Fall Meeting session MR32: Perspectives on the Planetary Interior at Multiple Scales: Reconciling Experiments, Simulations, and Observations, and I am going to present in session MR21: Advanced Experimental and Analytical Approaches in Minerals Studies.

- 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. In addition, 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.)