Expressions of interest for the ESRF-EBS and a long ID27 beamline

Contact
Denis ANDRAULT <denis.andrault@univ-bpclermont.fr>, LMV-UBP-CNRS, Clermont-Ferrand, France

Title and Scientific area
Matter at extreme pressures and temperatures

Expected characteristics for a long XRD extreme conditions beamline at ESRF-EBS
- 120 meters long beamline
- Tunable energy from 10-60 keV (tunable undulators; e.g. U20 with 4 mm gap)
- Switchable optics: o Pink beam optics (KB mirrors, multilayer coated for 0.5-2% BW)
  o Monochromatic beam optics (Si(111))
- Gain in flux: x50 (with energy resolution 10^{-4}) to x5000 (with energy resolution: 10^{-2})
- Variable focal spot size: 10 x 10 µm² down to 0.1x0.1 µm²
- Time resolved: Flux: 2 x 10^{10} ph/pulse @ 25 keV, 2 x 10^{9} at 50 keV (100 ps)
- Detector: large-area high energy pixel detector with 10 Hz readout (e.g. PILATUS/ CdTe)

Scientific case, including the justification for the request of ESRF-II capabilities

Introduction
Science at extremes conditions of pressure and temperature is a vibrant domain of international research that addresses fundamental questions in scientific disciplines as diverse as fundamental condensed-matter physics, Earth & Planetary sciences and materials science. In the last decade, several major international initiatives focused on extreme conditions tackled some of mankind's most pressing issues, for example, the deep carbon cycle in the Earth (DCO 2009) and the Energy Science project to search for future sources of energy (EFREE 2009). Such projects are also essential to establish a better understanding of planetary interiors, fundamental physics at extreme conditions, and to create new materials for energy harvesting and storage. For these reasons, science under extreme conditions was identified as one of the pillars of the scientific case for the EBS (see “orange book”).

Research at large scale facilities has always been at the leading edge of extreme conditions science. The exciting perspective of a new generation of diffraction-limited synchrotrons will allow the exploration of material properties at conditions far in excess of those currently achievable. Many of the major breakthroughs in extreme conditions research over the last two decades have occurred at 3rd generation synchrotron facilities. Indeed, compared to other large scale facilities, synchrotron radiation offers a unique diversity of state-of-the-art techniques for the characterization of matter. At the ESRF, the scope of this research field has been constantly expanding and developing, such that, remarkably, the structural, dynamical, electronic and magnetic properties of materials at pressure up to 100 GPa can now be determined with the same accuracy as if at ambient conditions.

The proposed ESRF source upgrade will provide for the X-ray diffraction beamline ID-27 significantly higher photon flux density and higher coherence, especially for photon energies above 30 keV, i.e. the energy range most relevant for diffraction and imaging at extreme conditions. These improvements will allow studies to be carried out on much smaller sample volumes and on much
shorter time scales. The direct impact on studies at extreme conditions is that higher pressure and temperature states which can be generated only in small volumes or in transient processes will become experimentally accessible. Breakthroughs can be expected in various scientific areas. Non exhaustive examples are briefly introduced below:

**Static route to ultra-high pressures:**

New designs of diamond anvil cells (DAC) are currently being developed by several groups, which aim at generating higher compressions with double-stage diamond anvils or modified shapes of diamond anvil tips obtained by micro-machining. These ultra-high pressure DAC (U-DAC) open the route to the extreme conditions found in natural systems such as stars, brown-dwarfs, large planets and exoplanets. Experiments at such extreme conditions have the potential to prove the existence of states of matter predicted by simulations, including electride-like solids, materials with bonded core electrons, metallic (fluid) hydrogen, and maybe discover new unexpected states...

Pressures in excess of 600 GPa have already been reached, which doubles the pressure domain available for static experiments. A new physics is therefore within reach, and adapted characterization techniques are required. Synchrotron X-ray diffraction (XRD) will play a central role as it provides primary information on the atomic arrangements of matter. In addition, XRD currently provides the only way of measuring the pressure reached in U-DAC experiments, based on the equations of state of calibrant materials.

U-DAC has a high pressure cavity of less than 5 µm in diameter. With no pressure medium, pressure gradients of several tens of GPa/µm occur at the center of the diamond culet (see Fig. 1). When a pressure transmitting medium is used, the available space for samples becomes even smaller. An X-ray beam much smaller than 1 µm is clearly needed to study properly the sample properties without a major signal from the surrounding material located at lower pressures.

**Time-resolved & nanoscale X-ray imaging under extreme conditions**

Major advances in X-ray imaging capabilities under extreme conditions have been recently achieved at the ID27 beamline, using the large volume Paris-Edinburgh press. (i) Implementation of a high-frame rate CCD camera for real-time X-ray radiography has opened the way to melt/liquid viscosity measurements using the falling sphere technique. Measurements have been successfully carried out on volatile-bearing silicates and iron alloy liquids. (ii) X-ray tomography (in both absorption and diffraction) has been developed thanks to an innovative rotation module (RoToPec) allowing a 360° access to the sample under conditions up to 10 GPa and 2500 K. This device provides a novel 3D probe of the evolution of microstructure, phase distribution, strain-state and volume changes of materials under extreme conditions.

The specifications of the ESRF-EBS opens new scientific opportunities. The nano-beam and ms time-resolution will enable time-resolved tomography for the investigation of ultralow viscosity liquids (\(\eta<10^{-3} \text{ Pa.s}\)), like CO\(_2\)-H\(_2\)O-NH\(_3\)-CH\(_4\) mixtures relevant for the dynamics of icy planets & satellites. The possibility to study solid-liquid segregation and melt migration in partially molten materials will open new routes to explore the dynamical processes of the deep Earth, like mineral dehydration, which is believed to be responsible for deep mantle seismicity in subduction zones and the generation of melt in the mantle wedge as a source for volcanic arcs.

The upgraded imaging station will enable determination of sample heterogeneities, with the ability to combine the nanoscale resolution with a large field of view. Moreover, exploiting the coherence of the beam, holographic techniques developed at ambient conditions will be applied for
Properties of light elements at ultra-high pressures; a focus on hydrogen

Since the predictions of a metallic atomic form of hydrogen at a density about 10 fold that of the cryo-solid at 1 bar, experimental studies have revealed the existence of four allotropes. The boundary lines between these phases have been disclosed by Raman and infrared measurements, but synchrotron XRD is mandatory to reveal their microscopic nature. Phase I adopts the hcp structure with freely rotating molecules. The structure was refined by single crystal diffraction at ESRF and the equation of state of solid hydrogen has been measured up to 120 GPa. Phase II is dominated by large and very asymmetric angular quantum fluctuations, making it difficult to point to a well-identified single classical structure. The measurements at pressures up to 200 GPa recently performed on ID-27 are still unfortunately too low to obtain constraints on the structure of phases III and IV. Major scientific questions remain to be solved, as numbered in Fig. 2: (1) the nature of phase III and IV, (2) the structural changes at the transformation from the molecular H$_2$ fluid to the plasma, with the possible existence of a first order transition, (3) the structure of metallic hydrogen and the nature of its associated discontinuities and (4) the possible existence of a low temperature metal fluid and its microscopic nature. A brighter beam with a focal spot less than 0.5 µm is mandatory for extracting the structural signal of a crystal of hydrogen of a few µm diameter above 250 GPa, because its X-ray scattering cross-section is so small.

Understanding the structural properties of liquid hydrogen at high pressure is also of fundamental interest since subtle structural changes in the liquid could explain the maximum on the melting curve. So far, most of the structural measurements in fluid hydrogen have been achieved near ambient pressure on mm size samples. Recently, the structure factors of liquid H$_2$ and D$_2$ have been successfully measured up to 5 GPa in the DAC at ID-27 thanks to the use of a multichannel collimator device. The combination of the greater focusing power of the long beamline proposed here, combined with the increased flux of ESRF phase II will allow these studies to be extended to the 100-200 GPa range in spite of the necessarily small sample sizes involved, minimizing the parasitic signal from the sample chamber.

Chemical analysis and study of phase relations: partial melting of geological materials

It is widely accepted that the early Earth was partially molten (if not completely) due to the high energy dissipated during terrestrial accretion. After core-mantle segregation, subsequent cooling of the magma ocean led to fractional crystallization into the primitive mantle. Melting relations of silicates and metal-silicate systems have been investigated by petrological and chemical analyses of samples melted at high-pressures and recovered to ambient conditions. In situ studies, however, are required to determine the pressure evolution of the solidus and liquidus temperatures. More excitingly, chemical analysis of the samples can now be performed in situ during the occurrence of phase transformations, chemical reactions or melting, using X-ray fluorescence (XRF) in the laser heated DAC. Chemical maps can even be retrieved to determine the distribution of various elements between the different sample fractions. In a pioneer work of this kind, we could already determine the solid/liquid Fe partitioning for the complete range of pressures and temperatures found in the primitive Earth’s mantle (Fig. 3). At the same time, X-ray diffraction registered at each analysis location provides the mineral phase data relevant to each nano-XRF measurement.

The development of this experimental technique, however, is largely limited by lack of spatial resolution of the X-ray beam currently available, compared to what is routinely achieved using the scanning electron microscope (SEM). With an X-ray spot of ~2 µm diameter at ID-27, we are losing
Properties of liquids at the conditions of deep planetary interiors

Recently, the experimental study of planetary materials (e.g., silicates and iron alloys) in their liquid state has become the topic of intense scientific competition. Indeed, it is now possible to retrieve relevant information such as the local structure and density from measurements performed at extreme conditions in the laser-heated diamond anvil cell \(^{18}\). This is a point of primary interest as the properties of the liquids are thought to control the structure of the terrestrial planets during the accretion and differentiation processes. Properties of silicate and iron-alloy liquids also play a major role in controlling the dynamics of planetary interiors. For example, the convection mechanism in the outer core (that produces the Earth’s magnetic field) still remains poorly constrained. Also, the degree of chemical heterogeneity of the Earth’s mantle remains unknown, because it has been mostly inherited from the crystallization mechanism of the early magma ocean, which remains largely controversial.

Studies of the properties of liquids under extreme conditions are however highly restricted, not only in terms of accessible pressures and temperatures, but also in terms of the physical properties that are measurable experimentally. Technical difficulties arise from the high mobility of liquids in the sample chamber, as well as the high chemical reactivity at extreme temperatures of the samples with the diamonds and the pressure transmitting medium \(^{19}\). It is therefore difficult to obtain thermo-elastic parameters such as compressibility, thermal expansion, the Grüneisen parameter, heat capacity and viscosity, and yet these thermodynamic properties are required to produce accurate structural and dynamical models of the interiors of the terrestrial planets, including the Earth. More generally, any study on liquids at static pressures above 150-200 GPa remains a major challenge, while these liquids are of primary interest for the understanding of newly discovered terrestrial exoplanets.

Such experimental hindrances can be overcome: the melts can be brought to extreme temperatures by pulsed or ramped lasers within a transient, but thermodynamically equilibrated state of a few microseconds \(^{20}\). However, in order to probe the liquid properties during short timescale, a more brilliant and highly focused X-ray source is required to allow the collection of the liquid diffuse scattering signal with sufficient statistics. The need for an upgraded source/beamline become even more critical for low Z liquids, such as silicate melts.

Multigrain 3D crystallography in the diamond anvil cell

Phase transformation, pressure, and temperature induce microstructural changes in materials. These include changes of grain size, orientation, and crystallographic phases inside a polycrystalline sample. Under high pressure, microstructures are relevant for the understanding of seismic wave propagation in the Earth’s mantle and core which can then be used to map dynamical processes such as convection. The study of the evolution of the microstructures is a key discipline within
material science because it is a strong predictor of the mechanical properties of materials. In recent years, the development of multigrain crystallography under high pressure 21 allows the tracking of the orientation, position and strain tensors of individual grains inside a polycrystalline. Recent experiments performed at the ID27 beamline 4 demonstrate that the method can also be used for the tracking of individual grains during dynamical processes such as phase transformations (Fig. 4). The method can also be used to follow sample microstructures during transformations, grain nucleation and growth, plastic deformation and recrystallization.

Currently, the collection of multi-grain crystallography data, including sample rotation and collection times on the detector, takes about 30 minutes. This collection time does not allow the study of dynamical processes at temperatures relevant to the Earth’s mantle that occur over time scales of seconds to microseconds. The improvement of ID27 in the framework of the ESRF-EBS will open a broad domain of in situ dynamical studies. To allow fast multi-grain crystallography data acquisition, it would require (i) a major increase of X-ray flux at the sample position (ii) the purchase of new detectors allowing fast data acquisition and smaller pixel sizes, and (iii) faster rotation stages. This fits perfectly with the plans for a long XRD extreme conditions beamline at ESRF-EBS.

![Figure 4: Multigrain crystallography performed at ~18 GPa and 880 K in the DAC: Orientations of individual grains of olivine monitored during the phase transformation to wadsleyite. White dots are orientations of individual grains. Colors represent an average orientation distribution in the sample.](image)


List of potential users supporting the project