Science under Extreme Conditions of Pressures and Temperatures at the ESRF

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Introduction

The last decades have witnessed an unprecedented surge in the study of matter and materials at extreme values of pressure and/or temperature. The fundamental importance of this research stems from the fact that high pressure can deeply modify chemical bonds and induce myriad changes in materials. Many breakthroughs have been achieved at synchrotrons worldwide, in fields ranging from earth and planetary sciences to fundamental physics, chemistry, and materials research, and even in the life sciences, where questions on life and biological function under extreme conditions have been studied.

At the ESRF, research under extreme conditions is performed at more and more beamlines, including BM01, ID9HP, ID18, ID20, ID24, ID27, ID28, BM23, and BM30B. The array of techniques, initially restricted to structure determination with X-ray diffraction, now also covers inelastic X-ray scattering, nuclear resonance, and absorption spectroscopy. In parallel, a sample environment laboratory provides a dedicated user support for sample preparation and during the experiment. This article, after a short introduction to this laboratory, will take you on a tour around the ring to present recent research highlights using the different techniques available at the ESRF.

State-of-the-art sample environment laboratory

In the past several years, the ESRF has invested heavily in state-of-the-art equipment to perform challenging diamond anvil cell loadings on-site, in a well-equipped and maintained laboratory close to the beamlines. The existence of this specialized support laboratory has had a very positive impact on a whole class of experiments.

The high-pressure support laboratory is equipped with 15 well-maintained diamond anvil cells, most of which are Le-Toulec-type with gas-driven membranes for pressure generation. These generally have 0.1 to 0.4 mm culet tips, suitable for pressures well above 100 GPa.

Figure 1: Gas loading system and its control interface.

They can be used with simultaneous resistive heating to temperatures up to 1300 K, with laser heating to above 5000 K, or with helium cryo-cooling to temperatures down to 4 K. To drill the gasket holes, an automatic spark eroder is available, but for challenging experiments, or when a non-metallic gasket is required, the laser drilling system was developed by the sample environment unit in collaboration with the ID27 team. It allows faster and more accurate machining, and drilling with high precision into non-metallic materials.

For high-pressure experiments with DACs, the use of the best hydrostatic pressure transmitting medium is fundamental in order to reduce the pressure gradients in the cell. A state-of-the-art versatile and fully automated gas loading system (GLS) from Sanchez Technology was installed in April 2010 (Figure 1) and has served for more than 200 successful gas loadings since. The system allows easy and rapid load-

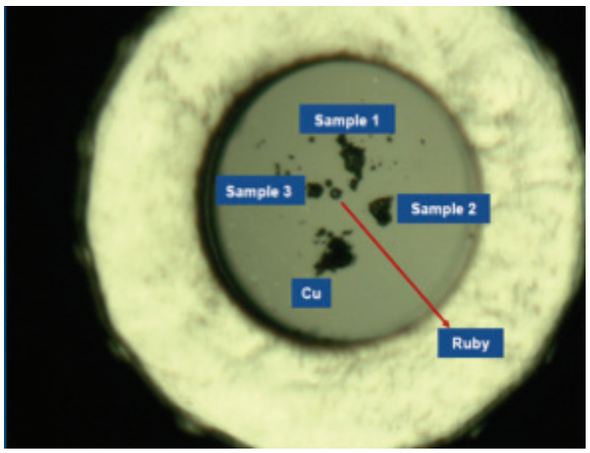

Figure 2: Top view of a helium-loaded DAC with three samples and two pressure markers (ruby and copper).

ing (~45 minute) of various gases (He, H_2, Ne, Ar, N_2); an example of helium loading is presented in Figure 2. Here, three samples together with two pressure markers are embedded in a helium hydrostatic medium. Off-line characterization equipment, such as a ruby fluorescence system for accurate pressure measurements and a micro-Raman spectrometer for fast chemical diagnostics, is available.

Diffraction

Beamlines ID09A and ID27

Beamlines ID27 and ID09A are devoted to determining structural properties of solids and liquids at high pressures and extreme temperatures with the greatest possible accuracy, using angle dispersive diffraction and area detectors. Although their technical capabilities largely overlap, some features are specific to each beamline: ID27 is optimized for ultra-high pressures (P > 150 GPa) and high temperatures (T > 5000 K) using laser heating. The CO_2 and YAG laser systems are permanently

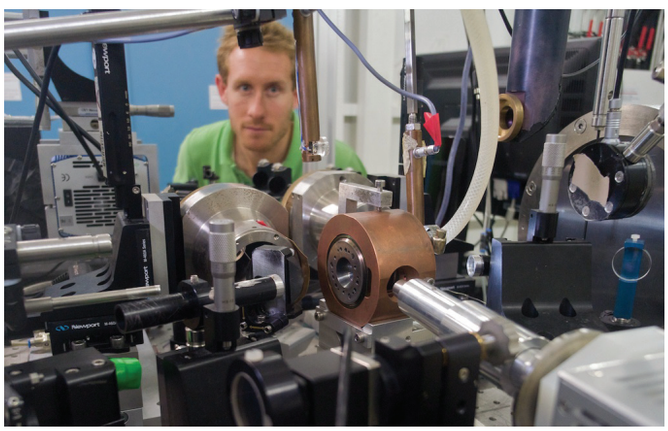

Figure 3: Micro-focusing bench of ID27 with DAC (center) and laser-heating set-up. Photo by Blascha Faust.

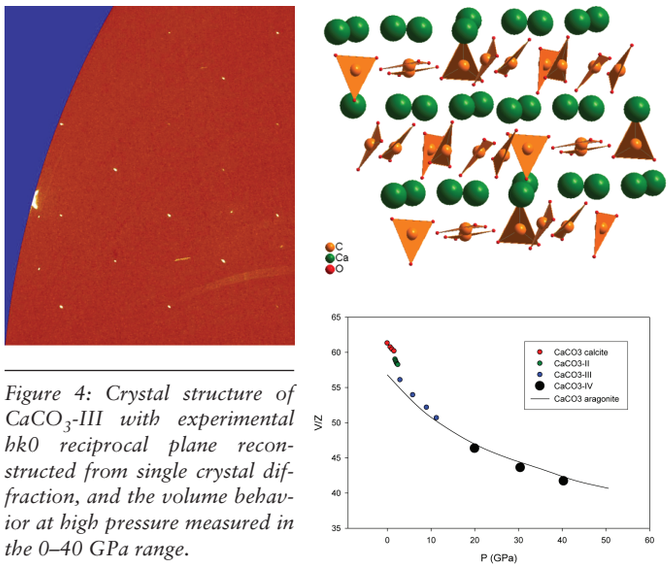

Figure 4: Crystal structure of $CaCO_3$-III with experimental hk0 reciprocal plane reconstructed from single crystal diffraction, and the volume behavior at high pressure measured in the 0–40 GPa range.

installed on a high-stability optical bench in the micro-focusing hutch. The very intense X-ray beam from two phased in-vacuum undulators is focused on a 2 × 3 μm^2 spot to probe very small, laser-heated samples. In the second hutch, a Paris-Edinburgh press allows researchers to simultaneously perform in-situ X-ray diffraction, absorption and diffraction tomography, density and viscosity measurements over a wide P-T range (P < 17GPa, T < 2500 K). ID09A supports powder diffraction well into the Mbar pressure range with the best possible resolution for 2D detection and at temperatures from a few K to 600 K. Over the same pressure and temperature range, single crystal datasets can also be collected for indexing; there is accurate refinement of the orientation matrix; crystal structure refinement (down to a few percent R_{Bragg}, depending on the sample quality); structure solution, for example by ab-initio or charge flipping methods (new structures have been determined after second-order and, in a few cases, also after first-order phase transitions). Orientation matrix of twinned or multiple crystals (i.e., 1–6 crystals) can also be successfully handled and integrated and data suitable for crystallographic analysis can eventually be extracted. Together with a user group, the ID9A team has started to develop laser-heated single crystal diffraction techniques [1].

New structures of $CaCO_3$ at high pressure

$CaCO_3$, one of the most common minerals, exhibits several high-pressure transitions, known for almost a century. However, the structures of the three high-pressure polymorphs in the 2–40 GPa pressure interval have been determined only recently [2] by optimized single crystal micro-diffraction at high pressure. The results show an increased complexity of crystal chemistry of carbonates at high pressure (Figure 4). Among the HP phases, $CaCO_3$-VI, occurring above 15 GPa (~440 km depth), may constitute an important carbon repository in the Earth's lower mantle, below the mantle transition zone.

Beamline BM01 (Swiss Norwegian CRG)

BM01 is devoted primarily to single-crystal diffraction and high-resolution powder diffraction/EXAFS. A Raman spectrometer is available for synchronized in-situ experiments, along with a Titan CCD detector (readout time ~1 sec) and a new multipurpose diffractometer featuring a 2M Pilatus detector (readout time ~3 msec). Area detectors are routinely used for in-situ powder diffraction studies at high temperatures and pressures, and with diamond anvil cells. The relatively large beam size (slit-adjusted to ~100 μm) allows for good powder data at lower pressures (<20 GPa).

Light hydrides: Promising materials for energy storage

A diffraction study of a hydride at various temperatures and pressures allows researchers to find new polymorphs, following their structural evolution and ultimately understanding and maybe even altering their thermodynamic stability. Recently, the first porous hydride was discovered, γ-$Mg(BH_4)_2$, showing 44% volume collapse upon compression. The high-pressure phase is a double-interpenetrated framework, forming via an intermediate amorphous state (see Figure 5). These observations offer an explanation of bonding schemes in complex hydrides and suggest a route to hybrid materials, exploiting the borohydride (BH_4) group as a ligand [3].

Inelastic scattering

Beamline ID28

Today, the inelastic X-ray scattering (IXS) beamline ID28 features an energy resolution between 1.3 and 6 meV with an efficient and modular focusing scheme, with a smallest spot size of 13 × 6 μm^2. The seven-meter, nine-analyzer spectrometer arm covers momentum transfers up to 100 nm^{-1}, and a versatile sample goniometry allows access to a large portion of reciprocal space. Plans for the future foresee installation of a dedicated set-up for diffuse scattering studies to be operated in parallel to the IXS spectrometer.

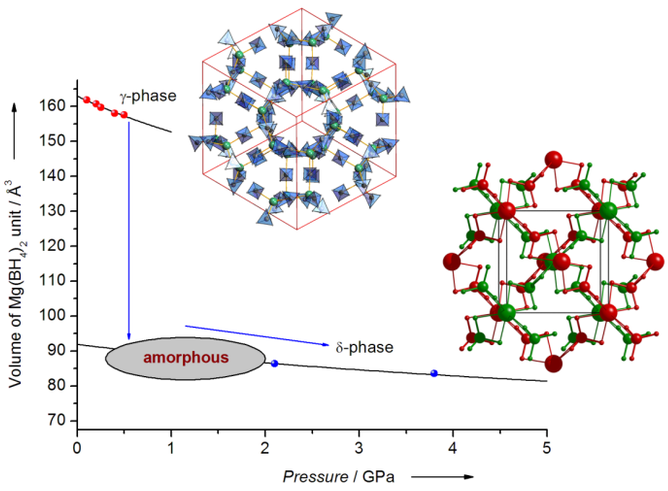

Figure 5: Pressure-induced transition from porous to dense magnesium borohydride framework, proceeding via an intermediate amorphous state.

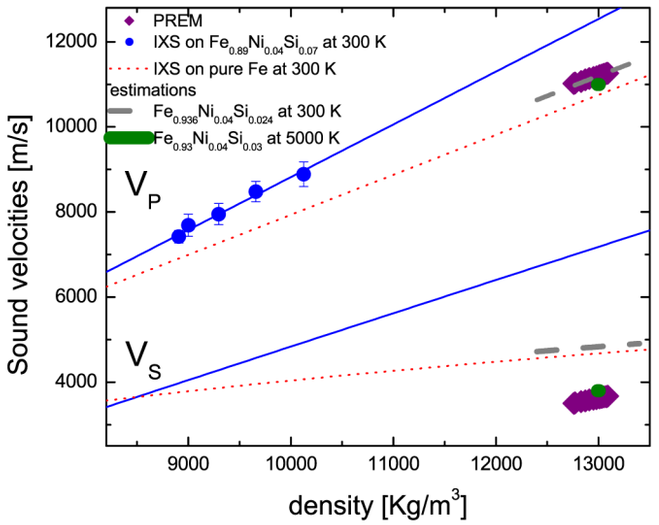

Figure 6: Aggregate compressional (V_P) and shear (V_S) sound velocity measurements on pure Fe (red) and Fe-Ni-Si alloy (blue). The comparison of this data with seismic observations (purple) supports an inner core model of Fe alloyed with Ni to 4–5 wt% and Si to 1–2 wt%.

Elastic properties and sound velocities of geomaterials

The Earth's interior cannot be directly sampled and is only remotely probed by seismology. Measuring the elastic properties and sound-wave velocities of geomaterials at pressures and temperatures characteristic of planetary interiors provides the necessary link between seismic observations and geophysical models. At ID28, these parameters were recently measured in the critical case of opaque samples, such as the iron-bearing oxides comprising the Earth's lower mantle [4] and iron alloys constituting the Earth's core [5] (Figure 6).

Future Beamline ID20

ID20 is a new beamline currently under construction which will significantly broaden the scope of the IXS program dedicated to the study of electronic excitations carried out at ID16 (for example, studies on ice under high pressure [6]), which was closed in 2011. ID20 will feature two spectrometers, one optimized for high efficiency with medium energy resolution (~300 meV), and the other for high-energy-resolution applications (~100 meV). An intense beam with a 16 × 8 μm^2 spot will allow studies at extreme conditions, as the optical configuration leaves enough free space around the sample for complex environments. ID20 will be open in 2013 and will offer a powerful complement to the existing portfolio of spectroscopy beamlines.

Nuclear resonance

Beamline ID18

The nuclear resonance beamline (ID18) allows studying samples under high pressure, high/low temperature and high magnetic/electric

fields. New X-ray optics at the high-resolution monochromator with 0.5 meV energy resolution at 14.4 keV (flux about 5×10^9 ph/s) and focusing optics with full aperture allow spot sizes on the sample of 5×10 μm^2. Recently, a grant from Germany (BMBF) made it possible to install a double-sided laser heating set-up for diamond anvil cells, opening perspectives to determine time-dependent properties using the pulsed laser source in combination with the pulsed synchrotron light and fast avalanche photo diode detectors.

Spin state of iron in lower-mantle perovskite

Measurements at a pressure of up to 110 GPa and 1000 K using a diamond anvil cell fitted with a miniature heater show that iron in lower-mantle perovskite is stable in a partial electron-paired configuration (intermediate spin state) throughout most of the lower mantle. The stability of the intermediate spin state may be related to the unusual environment of the iron atom in lower-mantle perovskite [7].

Absorption

Highly diluted XAS: Beamline BM30B (French CRG)

BM30B is devoted to the study of highly diluted samples, especially in the earth sciences, notably "hydrothermal fluids." This topic is at the intersection of the physical chemistry of supercritical fluids (intermolecular interactions and solvation processes in aqueous supercritical conditions) and hydrothermal geochemistry (transport and cycles of metals in geological fluids). A dedicated cell [8] allows XAS experiments in transmission and fluorescence modes while independently controlling pressure and temperature up to 1600°C and 0.2 GPa. This set-up is routinely used to characterize the speciation and solubility of elements of geological interest.

Aqueous complexes in hydrothermal conditions

The need of metals for industrial manufacturing has highlighted the importance of better understanding metal ore formation on both atomic and global scales. Scientists have performed concerted studies on relevant metals (Au, As, Sb, Ag, Cd) by combining in-situ XAS spectroscopy at BM30B with hydrothermal solubility experiments along thermodynamic and molecular modelling. The composition, structure, and stability of aqueous metal complexes in hydrothermal conditions up to 500°C and 600 bar are indeed critical knowledge. Particular efforts have been put into studies of gold speciation in hydrothermal fluids [9].

Microbial activity under pressure

Pressure is a key parameter for the large microbial populations in deep marine and terrestrial subsurface. As the effects of pressure on the biogeochemical processes to which bacteria contribute are barely understood, BM30B was used for a comprehensive study on the effect of high hydrostatic pressure on the rate and extent of bacterial dissimilatory metal reduction (DMR). This revealed DMR activity taking place up to 110 MPa, a value above the optimum pressure of growth, which points to possible biogeochemical activity in large submarine depths [10].

Energy dispersive XAS: Beamline ID24

The newly upgraded ID24 for energy dispersive EXAFS offers a focal spot of 3×3 microns^2, a flux of up to 10^7ph/pulse (~10^{14} ph/s in uniform mode), and soon a position-sensitive detector capable of recording a full spectrum every 2 microseconds. As it has no moving components, the spectrometer exhibits excellent stability and is particularly suited for HP investigations. It is possible to map (each pixel containing full XAS) the sample in the DAC at high spatial resolution [11]. A double-sided in-situ laser heating facility is available and the parallel, very fast acquisition of the spectrum in the full energy range makes possible dynamical studies (chemical reactions, diffusion processes) as well as studies of states of matter in states that can only be maintained very shortly. Future perspectives include investigation of electronic and local structure in laser-shocked matter at local thermal equilibrium and element selective magnetometry at the megagauss.

Radiolytic induced corrosion in nuclear reactors

The enhanced stability of the energy scale was exploited recently for in-situ studies of radiolytic-induced corrosion/oxidation in nuclear

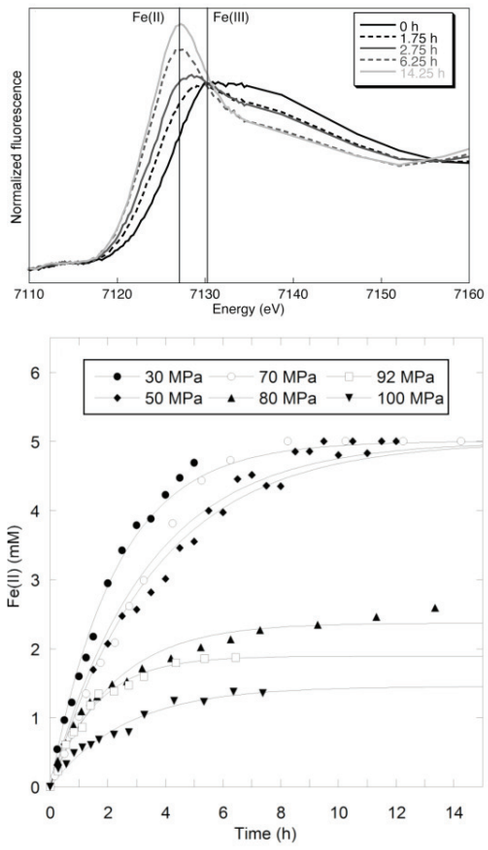

Figure 7: Fluorescence XANES in-situ measurements in a culture of S. Oneidensis MR-1, at 70 MPa/30°C, showing a progressive reduction from Fe(III) to Fe(II) with time (top). Production of ferrous iron over time as a function of pressure, derived from the XANES spectra (bottom).

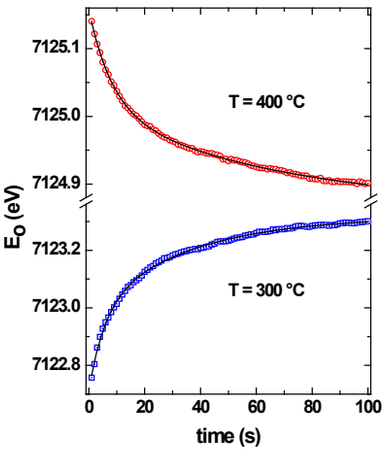

Figure 8: Fe K-edge energy (E_o) values, shown as points, as a function of time to 100 s, measured from a 0.69 m Fe(II)Cl_2 aqueous solution sample at 300 (due to oxidation of Fe^{2+}) and 400°C (due to reduction of predominantly Fe^{3+}). The solid lines are the fits to the E_o values used to determine kinetic data.

reactors. In-situ Fe *K*-edge XAS measurements were made on Fe(II)Cl_2 aqueous solutions to 500°C as a means to study the kinetics of high-temperature reactions of Fe^{2+} and Fe^{3+} ions with transient radiolysis species [12]. The radiolytic reactions in a DAC result in oxidation of Fe^{2+} at 300°C and reduction of Fe^{3+} and Fe^{2+} at 400–500°C. The edge-energy drift evident in the absorption data directly reflects the kinetics of reactions, leading to oxidation and/or reduction of the Fe^{2+} and Fe^{3+} ions in high P-T aqueous solutions (see Figure 8). The drifts are very small, but they are clearly detectable.

Pressure-induced suppression of ferromagnetism probed by XMCD

Today, polarized X-ray absorption is the only magnetic technique to probe virtually any element up to the Mbar range. Combining XANES and XMCD, simultaneous structural and magnetic information becomes available, which is very important in the high-pressure domain where the hydrostatic conditions are difficult to reproduce. XMCD has been efficiently applied at ID24 to study the complex interplay between magnetic, structural, and electronic degrees of freedom in the 3d metals at high pressure. Here, compression leads to a reduction of the density of states at the Fermi level to below the Stoner critical limit; suppression of ferromagnetism is therefore expected as well as possible associated structural transitions. In Co, recent work on ID24 provided the first experimental evidence of pressure-induced suppression of ferromagnetism around 120 GPa (Figure 10), in the range of the hcp phase instability versus the fcc phase [13].

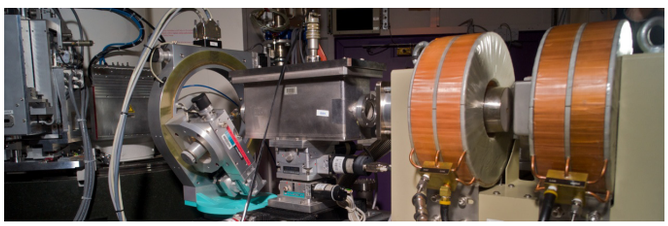

Figure 9: Set-up for XMCD measurements at ID24, with the micro-focus optics in the center and Helmholtz coils and the cryo-cooled sample to the right. Photo by Blascha Faust.

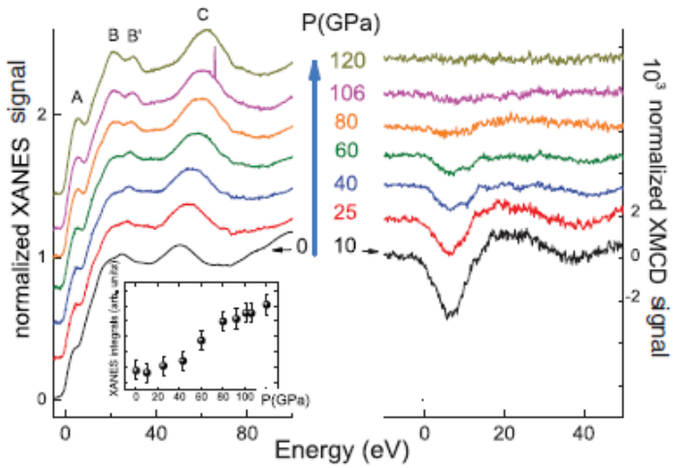

Figure 10: Normalized K-edge XANES (left) and XMCD (right) of Co as a function of P. Inset: Integral of XANES, illustrating the onset of the hcp-fcc phase transition around 80 GPa.

Ni was investigated up to 200 GPa, a record pressure for XMCD studies. XRD patterns recorded on ID27, combined with the XANES/XMCD data from ID24 (Figure 11), show that Ni is still fcc and ferromagnetism persists up to 200 GPa, in disagreement with the prediction of an abrupt transition to a paramagnetic state at these pressures [14].

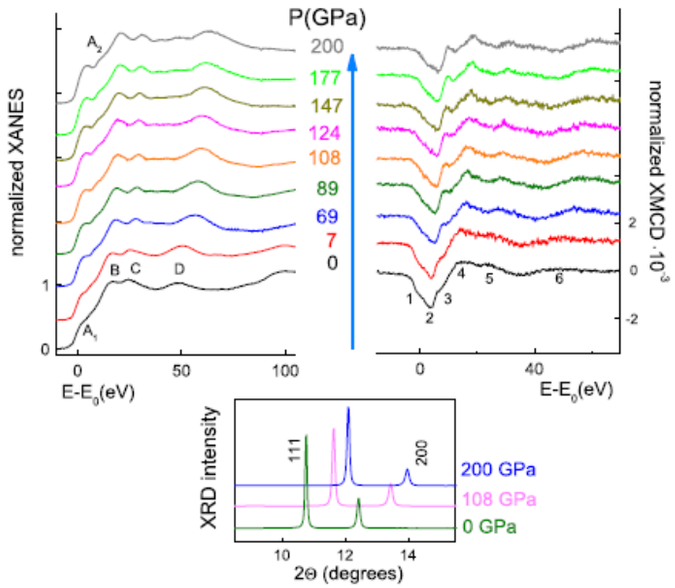

Figure 11: Combined XANES (left) and XMCD (right) on Ni up to 200 GPa. Selected angle-dispersive XRD integrated patterns (bottom).

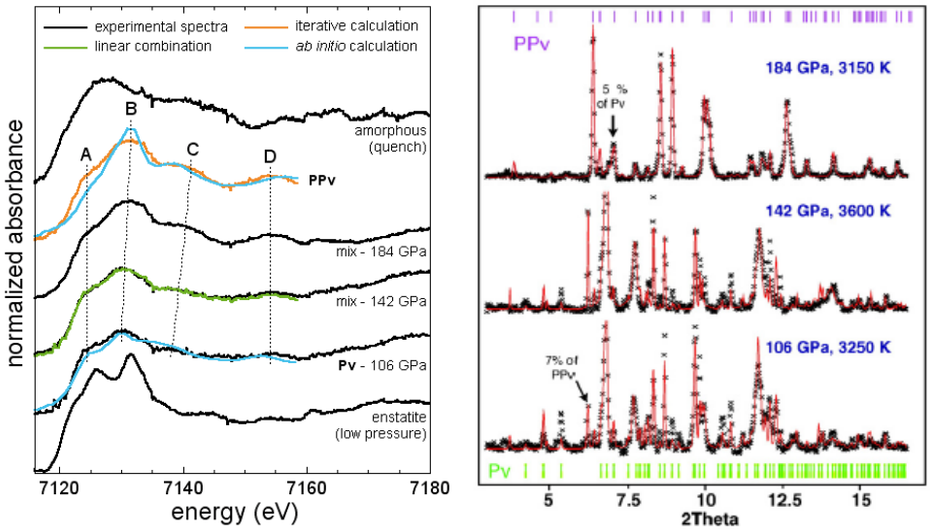

Figure 12: XANES (left) and integrated diffraction patterns (right) recorded for Al-bearing (Mg,Fe0.19)SiO3 Codera samples at P,T conditions of the core-mantle boundary.

Combined techniques

More and more experiments make use of several beamlines, each optimized for a specific technique. At the ESRF, beamtime can be allocated on two beamlines so that the users can carry a DAC from one beamline to another to measure a sample in identical thermodynamical conditions of P and T. This recently allowed scientists to deal with the fundamental geosciences problem of the origin of peculiar seismic features observed in the D”-layer, a 100–300-km-thick layer just above the core-mantle boundary. They used ID24 and ID27 in tandem to investigate minerals close to real earth composition. In particular, Al and Fe are known to modify significantly the phase diagram and elastic properties of the mantle minerals. By means of Fe K-edge XANES and X-ray diffraction (Figure 12), the fraction of coexisting perovskite and post-perovskite phases was investigated, together with the Fe distribution in a pressure domain extending from 100 to 185 GPa. Results suggest the coexistence of the two silicate phases throughout the whole D”-layer, with a post-perovskite phase largely depleted in Fe [15].

Conclusion and perspectives

Science at extreme conditions is a vibrant and dynamic interdisciplinary field that is one of the science drivers of the ESRF Upgrade Programme. Significant investments in instrumentation are underway to make possible extreme conditions research at beamlines where it was impossible before, such as on the EXAFS beamline ID24. This opens the door to a new generation of micro-second absorption experiments under very high pressure and/or high/low temperatures. Likewise, the new inelastic X-ray scattering beamline ID20, with a spectrometer equipped with over 70 analyzer crystals, is compatible with a laser heating system, making it possible to explore the electronic states of very hot and dense materials. These developments in phase I of the ESRF Upgrade Programme could be followed by the construction of a new high-brilliance low-emittance storage ring within phase II. The high-pressure diffraction beamlines would clearly benefit from the exceptional characteristics of such a new X-ray source currently under study. Its beam dimensions would be reduced by a factor of 2 with a flux density in the spot 30 times higher than today, making possible new science under extreme conditions with time-resolved experiments.

Acknowledgment

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