

Development of micro-XANES mapping in the diamond anvil cell

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Energy-dispersive X-ray absorption spectroscopy is now a well established method that has been applied to a broad range of applications. At the energy-dispersive EXAFS beamline of the ESRF, ID24, the recently achieved $5 \times 5 \mu\text{m}$ focal spot combined with fast acquisition has allowed complex and non-uniform samples to be mapped and images to be obtained where each pixel contains full XAS information. This method has been applied to a study under extreme conditions of pressure and temperature in a diamond anvil cell in transmission mode. The case study was the investigation of the Fe *K*-edge XANES of (Mg,Fe)SiO₃-perovskite and (Mg,Fe)O-ferropericlae on decomposition of the spinel-structured olivine [γ -(Mg,Fe)₂SiO₄] at 78 (3) GPa after laser heating at 2200 (100) K.

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1. Introduction

One of the major goals in geosciences is the study of the dynamics of the solid Earth and properties of each of the Earth's reservoirs. This requires a detailed knowledge of the properties of the main mineral phases which compose the Earth's mantle, core, subducting slabs and ascending plumes under pressure and temperature conditions that may exceed 150 GPa and 5000 K, respectively. The iron oxidation state, in particular, is an important factor governing the reservoir mineralogy, the material exchanges at the core–mantle boundary, and the exchange of oxygen between deep mantle and globe surface (Wood *et al.*, 2006; Rohrbach *et al.*, 2007). The study of chemical reactions of complex systems close to natural rocks under the actual conditions of the Earth's interior is essential for modelling the mineralogy and the chemistry of our planet. Although diamond anvil cells (DACs) associated with laser heating techniques allow us to reach such thermodynamic conditions, experiments under these conditions are usually associated with significant challenges. These include limited sample amount in the DAC (of the order of 10^{-10} g), pressure and temperature gradients, and the fact that several phase transitions are not quenchable. Moreover, pressure and temperature gradients give rise to a complex spatial distribution even inside the small volume of the DACs. A probe with micrometric spatial resolution, chemical sensitivity and allowing *in situ* investigation would fulfil the constraints of such types of experiments.

Visual observation, Raman and infrared spectroscopies, X-ray and neutron powder diffraction, and resistivity

measurements are widely used for *in situ* sample characterization in DACs and they certainly could recognize chemical reactions at high pressure. Raman and infrared active bands as well as diffraction patterns change on account of a chemical reaction or phase transformation of a material, but are neither chemically specific nor particularly sensitive to changes in oxidation states. On the other hand, Mössbauer spectroscopy is very sensitive to the chemical state of elements but lacks the spatial resolution necessary for studies of materials in the laser-heated DAC. There are also other different laboratory methods capable of determining the composition, chemistry and structure of complex heterogeneous materials, such as beam methods or scanning probe techniques (Adams *et al.*, 2005). These methods can achieve not only a nanometric lateral spatial resolution but also allow the analysis of a third dimension thanks to the depth resolution obtaining three-dimensional pictures that could describe the system taking into account the actual thermal gradient present in the laser-heated DAC. Unfortunately, these methods do not enable the products of chemical reactions to be studied *in situ* under extreme conditions and therefore are not suitable for the study of unquenchable structures and even less for the characterizations of reagents and products of chemical reactions during their evolution. Other techniques, based on the use of synchrotron radiation, such as X-ray fluorescence microprobes, combine micrometric spatial resolution and chemical analysis with the possibility of *in situ* experiments thanks to the physical penetration of hard X-rays, allowing a highly absorbing sample environment, such as DACs, to be used. Nonetheless, using these techniques it is currently impossible

to retrieve complete structural information. X-ray absorption spectroscopy (XAS) is a chemically selective spectroscopic technique and is able to provide information about structural and electronic properties such as number and distance of neighbours as well as oxidation state and chemical speciation (Rehr & Albers, 2000). The strength of XAS in dispersive geometry applied to science at high pressure is well documented in the literature (Itié *et al.*, 1989; Sapelkin *et al.*, 1996; Aquilanti & Pascarelli, 2005; San-Miguel *et al.*, 2007; Aquilanti, Trapananti *et al.*, 2007; Aquilanti, Libotte *et al.*, 2007). In fact, the inherent beam stability owing to the absence of movement of the optics during spectra acquisition and the small spot obtained, thanks to the focusing properties of the polychromator, match the size requirements of samples at high pressures. Moreover, on ID24 at the European Synchrotron Radiation Facility (ESRF) the choice of the source (undulators) allows the severe X-ray beam attenuation through the high-pressure cells to be overcome, especially at energies below 8 keV. Recently, the energy-dispersive XAS (EDXAS) beamline, ID24, has been used for μ -XAS applications with a micrometric spatial resolution obtaining two-dimensional XANES (X-ray absorption near-edge structure) maps where each pixel contains full XANES information (Pascarelli *et al.*, 2006). μ -XAS two-dimensional mapping has been used so far in fluorescence mode to investigate the content, redox and speciation of iron on a natural rock thin section (Muñoz *et al.*, 2006).

Potential future scientific opportunities include:

(i) Studies of dilute systems in highly absorbing environments (*i.e.* DACs) using fluorescence detection. For example, the flux at the Fe *K*-edge [of the order of 10^{14} photons s^{-1} (0.01% bandwidth) $^{-1}$ on ID24] allows for XANES characterization of relatively dilute samples (down to 1 wt% of iron for about 30 μ m-thick natural samples). Using specially designed DACs, where diffusion of X-rays from the environment are minimized, acquisition times of the order of seconds should be feasible.

(ii) Studies at extreme pressures and temperatures in DACs using *in situ* laser heating techniques.

In this article we illustrate a novel method for two-dimensional μ -XAS mapping in transmission mode through a DAC. The test case concerns a geological relevant issue under extreme conditions of temperature and pressure in a DAC. We show how this method can provide information, with micrometric spatial resolution, on the behaviour of iron during the reaction of decomposition of the spinel-structured olivine (O1) [γ -(Mg,Fe) $_2$ SiO $_4$] into (Mg,Fe)SiO $_3$ -perovskite (Pv) and (Mg,Fe)O-ferropericlasite (Fp). We underline that the aim of this article is to describe in detail the hardware set-up needed for performing such types of experiments. The analytical method for the data analysis is described by Muñoz *et al.* (2008). The interpretation of the results, together with the geological implications, will be given in a following paper.

2. Experimental details

The experiment was performed at the dispersive EXAFS (extended X-ray absorption fine structure) beamline of the ESRF, ID24. A sketch of the optical scheme can be found by Pascarelli *et al.* (2006). The X-ray source consists of three undulators with gaps adjusted to have the maximum of the first harmonic at the energy of the Fe *K*-edge (7112 eV). The X-ray source is then coupled to two silicon mirrors in a Kirkpatrick–Baez geometry at a grazing incidence angle of 3 mrad and to a Si (220) polychromator crystal in the Bragg geometry that disperses and horizontally focuses the beam to 5 μ m FWHM at the sample position. An additional Si mirror is placed downstream of the polychromator at a grazing angle of 4 mrad to vertically focus the beam down to 5 μ m FWHM. Fe *K*-edge XANES spectra were recorded in transmission mode using a fast CCD-based position-sensitive detector developed at the ESRF, *i.e.* the FReLon camera (Labiche *et al.*, 2007), in the energy range 7090–7210 eV. Pixel–energy calibration was based on the acquisition of XANES spectra of a metallic iron foil.

Fig. 1 shows a photograph of the experimental hutch of ID24 with the required set-up for such XAS experiments at high pressure. The DAC is mounted on a stack of motors allowing x – z alignment with respect to the beam as well as in the y direction in order for the sample to be positioned exactly at the horizontal and vertical focal plane. A well known short-fall of XAS experiments at high pressure using a DAC is the crystal structure of the single-crystal diamond anvils. In the specific case of an energy-dispersive XAFS experiment the polychromatic beam impinges on the sample with a wide energy bandpass (of about 100–500 eV presently at ID24 at the Fe *K*-edge, depending on the choice of the polychromator and focal length). These photons will inevitably cover energies that satisfy Bragg conditions for the crystal structure of the diamond. This causes X-rays to be diffracted off the polychromator–detector direction leading to large dips in the transmitted X-ray intensity I_1 . These dips, appearing as peaks in the spectrum as $\alpha = \ln(I_0/I_1)$, heavily spoil the data quality. For this reason the DAC often needs to be rotated along angles ω , χ and φ in order to shift the diamond Bragg peaks out of the energy region of interest. Whereas there are no

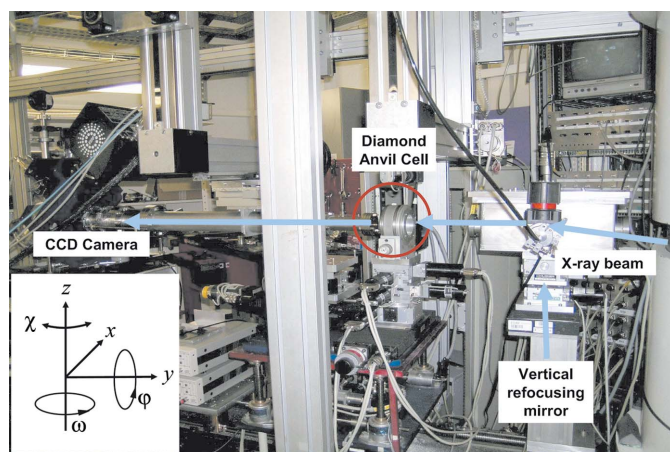


Figure 1

Experimental hutch of ID24 (ESRF) with the required set-up for μ -XAFS measurements at high pressure.

limitations for the angle φ , which can be rotated through 360° , both angles ω and χ are limited. Indeed, large values for ω and χ , on one side, would increase the effective thickness of the sample, not fulfilling the requirement for the EXAFS measurements, and on the other side decrease the effective gasket hole diameter. Acceptable values for these angles are up to $\pm 20^\circ$. For the angle χ this value further decreases down to $\pm 10^\circ$ because of the nature of the goniometer. This procedure can be very time-consuming when using energy-scanning XAS spectrometers. However, using EDXAS the transmitted intensity I_1 is visualized over the whole absorption spectrum energy range in ‘live’ mode. This allows the energy shift in the position of the Bragg peaks to be visualized in real time while rotating the DAC, until they are completely moved out of the energy range of interest.

As a starting material, a natural sample of San Carlos olivine with composition $(\text{Fe}_{0.12}, \text{Mg}_{0.88})\text{SiO}_4$ was used. Its chemical and phase homogeneity were confirmed by X-ray powder diffraction and microprobe chemical analysis. A double-sided polished irregular-shaped sample of thickness $25 \mu\text{m}$ was loaded into a hole drilled in a Re gasket, together with two small (about $2 \mu\text{m}$ in diameter) rubies. As a pressure-transmitting medium, Ar loaded under a pressure of 1.4 kbar was used. We employed diamonds with culets of height $300 \mu\text{m}$ and 1.6 mm. Fig. 2 shows a schematic diagram of the DAC with respect to the beam. The transmission of the X-rays through 3.2 mm of diamond ($\rho = 3.52 \text{ g cm}^{-3}$) in the energy range 7000–7500 eV is between 4.5×10^{-4} and 2.0×10^{-3} . The sample in the DAC was initially compressed to 78 (3) GPa and a portion of the sample of about $50 \times 75 \mu\text{m}$ was then double-side laser heated at 2300 (100) K using a YAG laser. Fig. 3 shows an optical image of the sample at 78 (3) GPa after the laser heating. The sample fills the gasket hole uniformly and the white part is the starting olivine pressurized to 78 (3) GPa while the dark rectangle represents the laser-heated portion of the sample. To record the XANES maps, the DAC was scanned horizontally and vertically in the focal plane of the X-ray beam with steps of $5 \mu\text{m}$. Fe *K*-edge XANES were recorded over a 50×50 step grid in order to cover an area of $250 \times 250 \mu\text{m}$. Each map contains 2500 XANES spectra (one spectrum per pixel). Given the high absorbance of the diamond anvils, the acquisition time was 4 s per spectrum. XAFS data reduction, including energy calibration, normalization and edge position tracking, was performed using

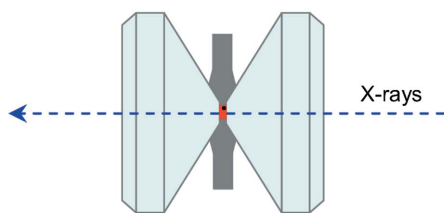


Figure 2 Schematic of the DAC. The dashed blue line represents the directions of the X-rays crossing the two diamond anvils. The sample (red rectangle) is held in place between the tips of the two diamond anvils by a metallic gasket. The diameter of the gasket is about $80 \mu\text{m}$. The black dot represents a small ruby used for pressure calibration purposes.

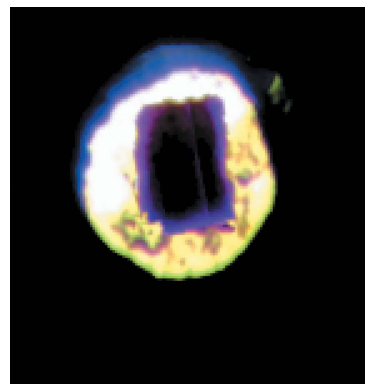


Figure 3 Optical image of the sample of San Carlos olivine compressed in Ar pressure-transmitting media at 78 (3) GPa. The dark rectangular area in the middle of the gasket hole is the part that is laser heated to 2300 (100) K.

the XASMAP software (<http://www.esrf.eu/UsersAndScience/Experiments/TBS/SciSoft/OurSoftware/XASMAP>), allowing different kinds of targeted maps, such as absorbance maps, at given energy to be obtained (Muñoz *et al.*, 2006). The analytical procedure to extract, from these maps, relevant information, such as the iron affinity for the different crystalline phases, is described by Muñoz *et al.* (2008).

3. Results and conclusions

Fig. 4 shows the two-dimensional maps of the normalized absorbance at $E = 7155 \text{ eV}$ after spectra normalization at 78 (3) GPa after laser heating. The choice of plotting the map of the absorbance at such an energy value is justified by the fact that at this energy the difference between the normalized

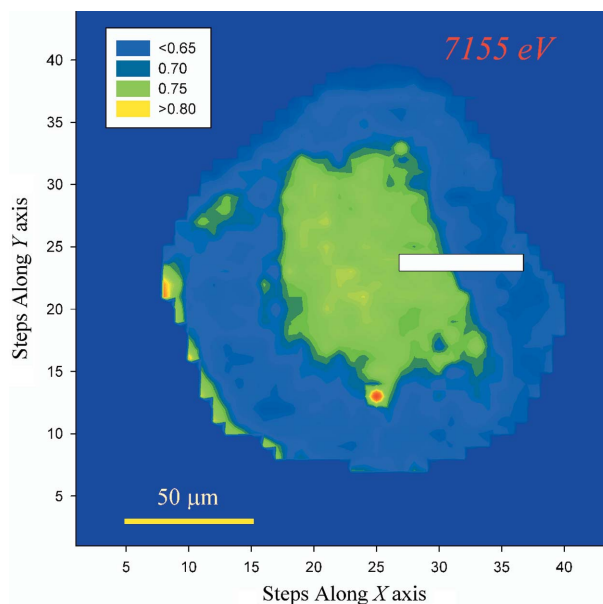


Figure 4 Absorbance maps at 7155 eV at 78 (3) GPa after the laser heating of the central part of the sample (green). The blue zone corresponds to the absorbance at 7155 GPa of the olivine compressed to 78 (3) GPa.

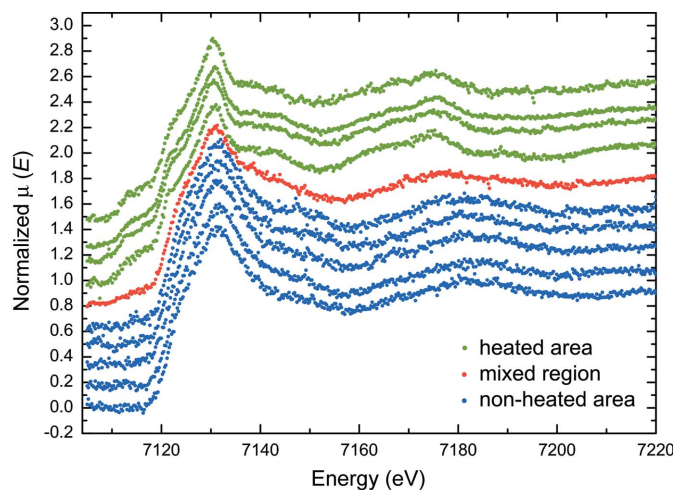


Figure 5

Normalized spectra of olivine in the non-heated area, in the mixed region, and of Pv and Fp assemblage in the heated area. The spectra are collected along the white line shown in Fig. 3 every 5 μm .

absorbance of the different specimens within the sample (Ol, Pv, Fp) around the Fe *K*-edge is maximum. The change in colour in the central part of the sample evidenced in Fig. 3 demonstrates a change in the absorbance within the heated zone probably due to a transformation from Ol into Pv and Fp. The red point corresponds to the position of one ruby sphere. Fig. 5 shows, from bottom to top, several normalized spectra of olivine in the non-heated area (blue spectra), the mixed region (red spectrum) and of Pv and Fp assemblage in the heated area (green spectra). The spectra are collected along the white line shown in Fig. 4 every 5 μm , that is the spatial resolution currently available at ID24. Only one spectrum shows the signature of a mixed phase between olivine and the Pv and Fp assemblage. The feature in the pre-edge region of the spectra recorded in the heated area cannot be assigned either to Pv or to Fp and this will be discussed in a following paper.

To conclude, we have shown that μ -XAS two-dimensional mapping recently developed at the energy-dispersive EXAFS beamline of the ESRF can be applied to study geological relevant issues under extreme conditions in a DAC, assessing,

with micrometric spatial resolution, the chemistry of individual high-pressure phases under equilibrium conditions in complex chemical systems. As a further development of this technique, we envisage the characterization of diffusion processes under extremes conditions and access to metastable states, by exploiting the time resolution naturally offered by EDXAS. Finally, a modification of the geometry of the ID24 spectrometer foreseen in the near future will allow the energy bandpass to be increased at energies below 8 keV up to $k = 20 \text{ \AA}^{-1}$ enabling the important step from μ -XANES to μ -EXAFS two-dimensional mapping to retrieve the full structural information achievable from the EXAFS features.

References

- Adams, F., Van Vaeck, L. & Barret, R. (2005). *Spectrochim. Acta*, **B60**, 13–26.
- Aquilanti, G., Libotte, H., Crichton, W. A., Pascarelli, S., Trapananti, A. & Itié, J.-P. (2007). *Phys. Rev. B*, **76**, 64103.
- Aquilanti, G. & Pascarelli, S. (2005). *J. Phys. Cond. Matter*, **17**, 1811–1824.
- Aquilanti, G., Trapananti, A., Minicucci, M., Liscio, F., Twaróg, A., Principi, E. & Pascarelli, S. (2007). *Phys. Rev. B*, **76**, 144102.
- Itié, J. P., Polian, A., Calas, G., Petiau, J., Fontaine, A. & Tolentino, H. (1989). *Phys. Rev. Lett.* **63**, 398–401.
- Labiche, J.-C., Mathon, O., Pascarelli, S., Newton, M. A., Guilera Ferré, G., Curfs, C., Vaughan, G. & Homs, A. (2007). *Rev. Sci. Instrum.* **78**, 91301–91312.
- Muñoz, M., De Andrade, V., Vidal, O., Lewin, E., Pascarelli, S. & Susini, J. (2006). *Geochem. Geophys. Geosyst.* **7**, Q11020.
- Muñoz, M., Pascarelli, S., Aquilanti, G., Narygina, O., Kurnusov, A. & Dubrovinsky, L. (2008). *High Press. Res.* **28**, 665–673.
- Pascarelli, S., Mathon, O., Muñoz, M., Mairs, T. & Susini, J. (2006). *J. Synchrotron Rad.* **13**, 351–358.
- Rehr, J. J. & Albers, R. C. (2000). *Rev. Mod. Phys.* **72**, 621–654.
- Rohrbach, A., Ballhaus, C., Golla-Schindler, U., Ulmer, P., Kamenetsky, V. S. & Kuzmin, D. V. (2007). *Nature (London)*, **449**, 456.
- San-Miguel, A., Libotte, H., Gauthier, M., Aquilanti, G., Pascarelli, S. & Gaspard, J.-P. (2007). *Phys. Rev. Lett.* **99**, 015501.
- Sapelkin, A. V., Bayliss, S. C., Lyapin, A. G., Brazhkin, V. V., Itié, J. P., Polian, A., Clark, S. M. & Dent, A. J. (1996). *Phys. Status Solidi B*, **198**, 503–508.
- Wood, B. J., Walker, M. J. & Wade, J. (2006). *Nature (London)*, **441**, 82.