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An *in situ* approach to study trace element partitioning in the laser heated diamond anvil cell

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Data on partitioning behavior of elements between different phases at *in situ* conditions are crucial for the understanding of element mobility especially for geochemical studies. Here, we present results of *in situ* partitioning of trace elements (Zr, Pd, and Ru) between silicate and iron melts, up to 50 GPa and 4200 K, using a modified laser heated diamond anvil cell (DAC). This new experimental set up allows simultaneous collection of x-ray fluorescence (XRF) and x-ray diffraction (XRD) data as a function of time using the high pressure beamline ID27 (ESRF, France). The technique enables the simultaneous detection of sample melting based to the appearance of diffuse scattering in the XRD pattern, characteristic of the structure factor of liquids, and measurements of elemental partitioning of the sample using XRF, before, during and after laser heating in the DAC. We were able to detect elements concentrations as low as a few ppm level (2–5 ppm) on standard solutions. *In situ* measurements are complimented by mapping of the chemical partitions of the trace elements after laser heating on the quenched samples to constrain the partitioning data. Our first results indicate a strong partitioning of Pd and Ru into the metallic phase, while Zr remains clearly incompatible with iron. This novel approach extends the pressure and temperature range of partitioning experiments derived from quenched samples from the large volume presses and could bring new insight to the early history of Earth. © 2012 American Institute of Physics. [doi:10.1063/1.3680573]

I. INTRODUCTION

In situ chemical analyses, especially elemental partitioning or diffusion at high pressure and high temperature, are scarce due to technical challenges and lack of appropriate measuring techniques. Coupling different analytic probes during time resolve experiments can greatly improve the comprehension of chemical properties in many fields such as geosciences, physics, and biology under pressure. In the present article, we describe the advantage of the combination of x-ray fluorescence (XRF) analysis coupled with state of the art x-ray diffraction (XRD) technique at high pressure. The technique was successfully applied to geological material relevant for the early Earth's history and could benefit to the all high pressure community.

Earth's early history has been constrained by a variety of studies, ranging from geochemical analyses of mantle and meteorite samples, cosmological and geophysical modeling, and experiments at high pressure and high temperature.^{1–3} One of the long lasting problem concern the fate of highly siderophile elements (HSE), including the platinum group (Pt, Pd) and heavy metals (Ta, Re, Au, W, and Os), that should be enriched in the Earth's core, due to their high affinity to iron,^{4,5} compared to the siliceous part of the Earth. However, their concentrations seem to be elevated in the Earth's mantle and crust compared to what can be expected from early partition coefficients experiments.⁶

Two hypotheses have been proposed in order to explain the discrepancy described above: (i) meteoritic bombardment at 100 ± 50 My created a late chondritic veneer that raise the concentration of siderophile elements in the mantle to its currently observed values;⁷ (ii) Alternatively, the enrichment of siderophile elements in the mantle could also be explained by a change of the metal-silicate partitioning coefficient of HSE, with a decrease of the siderophile affinity with increasing pressure.^{8,9} In order to test these hypotheses, siderophile element partitioning between molten iron and silicates must be determined at simultaneously high pressure and high temperature, preferably *in situ*. Partitioning data for the HSE are scarce as the experiments are very demanding.

Here, we present a new experimental setup that extends the capabilities for measuring partitioning coefficients to very high pressures and temperatures, in access of 50 GPa and 4200 K. The setup includes (i) a specially designed diamond anvil cell (DAC) that allows *in situ* spectroscopy by means of x-ray fluorescence collected at 90° from the incoming x-ray beam in the plane of polarization, as well as wide angle x-ray diffraction (ii) double sided laser heating with *in situ* time dependent temperature measurements and (iii) an optimized polycapillary optic enhancing the XRF signal in comparison to the background,¹⁰ and thus allows elemental mapping of the sample in the DAC. This new experimental setup that represents an very advanced setup for *in situ* spectroscopy at HP-HT in the DAC, and offer new opportunities to probe experimentally new deep mantle chemical processes.

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FIG. 1. (Color online) (a) Photograph of the XRF set-up on ID27 at the ESRF. (b) Schematic drawings of the diamond anvil system designed for the experiment. The same color code is used on both pictures to highlight in red the YAG lasers paths, in yellow the x-ray incoming beam, in blue the solid angle available for XRD, in green the solid angle for XRF, and in orange the path for the temperature measurement.

II. DIAMOND ANVIL CELL TECHNIQUES

The DAC used for this experiment is based on the resistive DAC recently developed for XRF measurements in aqueous solution at ID22 (ESRF, France).¹¹ In the present study, we used high tungsten carbide seats to open a space on the side of the DAC to enable XRF detection at 90° from the incoming beam. In addition, an asymmetrical diamond anvil pair was mounted on the seats of the DAC. The downstream side was equipped with a 300 μm culet diamond displaying a boehler-almx¹² conical cut to ensure maximum access to reciprocal space with the XRD. The upstream diamond consists of a large flat anvil with a culet size of 1 mm and a height of 2.2 mm. Such anvil geometry indents and deforms the rhenium gasket only on one side—toward the smaller anvil positioned downstream from the beam—and therefore gives access to the XRF signal upstream from the beam, below the Rhenium gasket. The XRF signal is collimated by the polycapillary and detected by the vortex detector (Fig. 1(b)). This geometry enables optimal measurement conditions and reduces the Compton and Rayleigh scattering from the diamond anvils significantly.

In order to ensure continuous measurements upon laser heating, the DAC is cooled down using a circulation of water in a copper jacket around the DAC. This system avoids movements of the DAC that could be caused by the thermal expansion during laser heating. As a consequence the cell is not moving during the laser heating process when it is carried out smoothly by ramping up slowly the power of the lasers. In addition, the movements of the DAC can be tracked visually by following: (i) the rims of the hole and (ii) the position of the entrance of the spectrometer relative to the laser spots on the control screen (see Sec. II B).

A. Samples and loading

The starting material was made of an iron alloy foil (Fe90Ni10) and a synthetic silicate glass typical of the chondritic mantle composition (35.1 wt.% MgO, 3.3 wt.% CaO, 8.5 wt.% FeO, 3.4 wt.% Al₂O₃, 49.6 wt.% SiO₂).¹³ The glass

was crushed and grinded to fine powder ($\leq 1 \mu\text{m}$) and doped with 1000 ppm of Pd, Ru, and Zr. While the Pd and Ru are known to be highly siderophile, Zr is highly lithophile. The presence of both types of elements enables a clearly distinct geochemical behavior. The starting chondritic material was heated at 1273 K for 12 h in a vacuum oven for the purpose of dehydration. Finally, the powder was re-sintered in a Paris-Edinburgh press at 1–2 GPa and 1073 K for 4 h. The samples were loaded into a 120 μm diameter hole of a rhenium gasket in such a way that a chip of (a) sintered doped glass and (b) a thin foil of iron-nickel were sandwiched between two MgO pellets. Thus, we used MgO as a pressure transmitting medium, thermal insulator and internal pressure standard. During loading the chondrite glass and the iron alloy were carefully positioned so that they partially overlapped and could be separated through the XRF into three distinct areas, (a) one with only glass, (b) a second with only metal, and (c) a third that produced XRF signals from both materials that are in contact with each other.

B. Laser heating

Two fiber lasers (photonics spectra physics®) emitting laser light with a wavelength of 1064 nm and providing a maximum total power of 220 W, were used to heat each side of the DAC sample. Both lasers were defocused in order to enlarge the heating area to about 30 μm , resulting in an enlarge profile, ensuring a homogenous heating of this large sample volume. Temperature was measured at the centre of the hot spot by analyzing the pyrometric signal emitted on a $3 \times 3 \mu\text{m}^2$ area using a 300 mm Acton equipped with a Pixis 100 spectrometer from Princeton instruments®. The pinhole (50 μm diameter) at the entrance of the spectrometer was aligned to the x-ray spot using the visible fluorescence induced by the interactions between x-rays and the Rhenium gasket, few micrometers on the side of the sample chamber. This pinhole is also used as a visual guide when aligning both lasers on the sample surface. Temperatures were calculated using a Wein function by the “SHADE OF GREY” software.¹⁴

III. BEAMLINE SETUP

Data were collected at the high pressure beamline ID27 at the European Synchrotron Radiation Facility (ESRF), Grenoble, France.¹⁵ The monochromatic beam ($E = 33 \text{ keV}$) was focused to a FWHM spot of $2 \times 1.7 \mu\text{m}^2$ using an Ir-Al multilayered Kirkpatrick-Baez (KB) double mirror bender (Fig. 1(a)). The total flux in the focal spot was about 2×10^{11} photons/s. To collect x-ray diffraction patterns, the beam was cleaned using a pinhole with an opening of 30 μm . For fluorescence measurements, this pinhole was removed to get maximum flux for good statistics in a reasonable time period. The incident flux of the focused beam was continuously monitored using an ionization chamber placed downstream of the KB mirror system.

The set-up at ID27 also enables to move the x-ray beam across the laser spot, without significantly changing any other optical alignments, by changing the tilt of horizontal x-ray

focusing mirror of the KB system. This capability allows the collection of XRF and XRD patterns at different positions in the laser spot while maintaining constant P and T on the sample. We used this technique to measure XRD/XRF patterns (see below) in the center of the laser spot, at 5, and 10 μm away from the center of the laser hot spot.

A. X-ray diffraction analysis

Diffraction patterns were collected with the MarCCD®, located at 214 mm from the sample. Debye-Scherrer rings were integrated using the FIT2D software.¹⁶ X-ray diffraction patterns were collected to determine the sample pressure, identify the appearance of new phases and to monitor the onset of melting based on disappearance of the diffraction lines and appearance of x-ray diffuse scattering.

B. X-ray fluorescence analysis

The x-ray fluorescence signal was collected by a single element Vortex® (SII NanoTechnology USA Inc.) silicon drift detector (SDD) located at 90° from the incoming beam in the polarization plane (Fig. 1(b)). This geometry is especially advantageous for detection of fluorescence signals, since elastic and inelastic scattering are minimized, and therefore the signal to noise ratios is optimized. For an optimal detection, e.g., to significantly reduction of the rhenium signal (gasket material), the cell has to be turned counterclockwise by 8°. The detector was equipped with a polycapillary, made by XOS®, with a working distance of 50 mm especially developed for DAC studies on dilute elements. The characteristics of this polycapillary collimator, such as its efficiency, are well described in a recent study.¹⁰ So far, the detector capillary has only been used for excitation energies below 20 keV, and Figure 2 illustrates the great advantage of using this confocal optic for XRF even with a high energy incident beam of 33 keV. For comparison, the XRF signal emitted by the sample was also measured with a regular collimator used on ID22 for high energy XRF. This collimator could not be placed at its optimal working distance of 15 mm, but at the best position for such DAC studies at about 35mm. Using the detector polycapillary, the signal to background ratio can be improved by one order of magnitude due to the strong reduction of the

Compton scattering originating from the diamond-anvil when using high energy x-rays.

All XRF spectra were acquired in ≤ 50 s during the time resolved measurements and mappings. Prior to the actual measurements on the sample, we performed tests on a standard solution containing 1000 ppm of Pd, Ru and Zr using collection times of 300 s. Peak areas of the detected elements were determined by fitting the spectra with the PYMCA software.¹⁷ Minimum detection limits (MDL) were calculated for each element according to the following formula:

$$C_{MDL,i} = \frac{3 \cdot \sqrt{I_B}}{I_i} \cdot \frac{\sqrt{t}}{\sqrt{1000}} \cdot C_i, \quad (1)$$

with I_B is the intensity of the background, I_i is the intensity calculated from the area under the $K\alpha$ peak of the element i integrated over the $\pm 3\sigma$ zone, t the collection time and C_i the actual concentration of element i . I_B and I_i were calculated using the PYMCA software. MDLs are the theoretical minimal elemental ($C_{MDL,i}$) concentration detectable with this setup, and were determined to be 2 and 3 ppm (± 0.1 ppm) for Zr and Ru, respectively. We were not able to calculate MDL for Pd as it disappeared from the solution probably due to some reactions with the gasket or the needle used for loading the solution. Still, we estimate the MDL of Pd to be close to the one of Ru as the two elements exhibits a fluorescence cross section very similar at 33 KeV.

IV. IN SITU XRF MEASUREMENTS AND RESULTS

For each loading, a region of interest was selected prior to laser heating by mapping and/or scanning the interface between the metal foil and the chondritic glass sample using their respective XRF signals, i.e., a strong signal of Fe in the metallic foil, or Pd, Ru, and Zr in the chondritic glass. Thus, the interface was identified when the intensity of iron XRF peak increased as the trace elements signals decreased. We determined the optimal position for laser heating when the XRF signal was nearly free of Pd, Ru, and Zr. At this position, the sample volume excited by the incident x-ray beam is entirely located within the iron foil but as close as possible to the interface of the chondritic glass. After performing an initial measurement of the elemental partitioning using XRF mapping, both infrared lasers were aligned to the position of the x-ray focused beam. Thanks to the defocusing option of the laser optics, laser spots with a diameter of up to more than

FIG. 2. (Color online) XRF spectrum collected in the chondritic sample with a regular collimator and the polycapillary. (a) The intensities are reported in logarithmic unit. (b) Intensities are shown with a linear scale, the gain of the signal to background ratio is about on order of magnitude for the trace elements of interests Zr, Ru, and Pd.

FIG. 3. (Color online) *In situ* evolution of the XRF signal with time, recorded at different temperature steps, for two different samples. In both figures, squares represent the intensity of Ru, circles refer to Pd intensity and diamonds indicates the Zr intensity. (a) Sample Cell05 was cold compressed to 10 GPa before laser heating. Three XRF spectra were collected every 50 s in the center of the laser. (b) Results for sample Cell02. Dark symbols are XRF intensities at the center, in grey at 5 μm , and in light grey at 10 μm away from the hot spot.

30 μm diameter were achieved and we could perform heating of both parts of the sample at their interface. Temperature was also measured at the x-ray spot. The laser power was increased until complete melting at the interface between the two samples occurred until complete melting was detected as evidenced by the disappearance of the diffraction peaks of iron and the appearance of diffuse scattering. Different experimental strategies were tested to retrieve kinetic and spatial information on the element concentrations as described below.

A. Kinetic measurements

For some experiments, we collected several XRD and XRF spectra at each temperature in order to probe the distribution. For run Cell05 (Figure 3(a)), the sample nominal pressure was 13 GPa and rose up to 15 GPa, due to thermal expansion induced by the laser heating. The intensity of each element has been re-normalized to palladium using their fluorescence cross section at 33keV.¹⁸ The evolution of the intensity is monitored as a function of time while the sample is heated up. At 2100 K, the melting temperature of the metallic foil¹⁹ but below the melting temperature of the silicate phase at ~ 2300 K,²⁰ limited increase of the fractionation is visible. At 2300 K, melting can be clearly identified in the diffraction pattern, with the appearance of diffuse scattering, and the fractionation becomes pronounced as evident in the raising XRF signal of Pd and Ru. The increase of concentration of the elements into the metal then becomes clearly visible as melting takes place. It is evidenced by an increase in the intensity of the siderophile elements of Pd and Ru in the metal as a function of time. On the other hand, the concentration of Zr in the metallic foil remains nearly unchanged, due to the lithophile character of Zr.

In case of sample Cell02, we scanned the x-ray beam laterally across the sample during the laser heating experiment (Figure 3(b)). For this sample, we determined a nominal pressure of 22 GPa that rose up to 25 GPa upon heating. One could interpret the resulting concentration profile as a diffusion profile between molten silicate and metal, measured as a function of time *in situ* during the laser heating in the DAC. The results show very fast diffusion of the trace element at the first sign of melting above 2700 K. At 4000 K the concentration of siderophile elements is low at the center of the laser spot and significantly higher at 5 to 10 μm away from the center of the laser spot, in the metallic foil. While this measurement is in clear agreement with the siderophile character of Pd and Ru, it remains difficult to interpret the concentration/diffusion profiles quantitatively. In particular, the trace elements appear to be depleted in the center of the laser spot at very high temperature. This could be attributed to migration of molten silicate and metals in the laser spot. Further evaluation of the quenched sample is necessary to ultimately understand the processes taking place in the molten area. At this point, extracting partitioning coefficient *in situ* remains too difficult. As described above, when melting appears, phase relations become very complexes and quantification nearly impossible. Meanwhile, classical approach on quench sample can still be used by choosing the right probe to measure the recovered samples; we describe such an approach below.

B. Samples mapping

In situ experiment ended with fast quenching through cutting off the power to the laser. We finally carried out XRF mapping of the quenched sample area that experienced melting at high pressure and temperature. An example of such elemental partitioning map is presented in Figure 4 for sample Cell02. The step size used for this mapping is 2.5 μm , thus of

FIG. 4. (Color online) Elemental mapping of Ru, Zr, Pd, and Fe *in situ* at 22 GPa. The center displays a picture of the sample taken after laser heating, where the location of the laser spot is indicated in white and the area mapped after quenching in the black square. The scales reported for each maps refer to the XRF intensity for each element.

the same dimension as the x-ray beam size in both directions. Elemental partition maps definitely indicate a higher concentration of Pd, Ru and Fe in a sharply defined area coinciding with the center of the laser hot spot. This observation is compatible with the *in situ* measurement, showing that Pd and Ru contents increase in the metallic foil as a function of time. After mapping, the pressure was released and the sample recovered for further quantitative analyses.

V. CONCLUSION

We described a novel experimental approach that offers unique capabilities for probing kinetics of phase reactions and partition *in situ* at simultaneous high pressures and temperatures. It is suited to provide information on non-recoverable and/or metastable high-pressure phases and avoids problems that can occur due to quenching of the sample. The ability to move the x-ray spot during laser heating is essential in these experiments, since it allows scanning across the sample interface. Such a feature could also be used for *in situ* mapping by changing the tilts of the two focusing mirrors, within the laser heated area. Therefore, it provides unique spatial information about material migration and elemental partitioning within a sample.

Accurate determination of trace element partitioning *in situ*, at simultaneous high P and T, remains difficult. While we achieved accurate calibration of the detector setup, thought the use of standards using a procedure described in previous DAC studies,^{21,22} the formation of micro-nuggets or sub-micrometers features in the silicate melt²³ could lead to misinterpretation on the partitioning coefficient. Thus, extra analyses of the quenched sample with additional techniques (e.g., FIB, SEM, TEM, nano-XRF...) would probably give more information to understand the *in situ* chemical partition reported in this study. Finally, the results from this DAC study will be compared with existing partitioning experiments conducted in large volume presses at lower pressures.

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