

Experiment Report Form

The double page inside this form is to be filled in by all users or groups of users who have had access to beam time for measurements at the ESRF.

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The Review Committees reserve the right to reject new proposals from groups who have not reported on the use of beam time allocated previously.

Reports on experiments relating to long term projects

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Should you wish to make more general comments on the experiment, please note them on the User Evaluation Form, and send both the Report and the Evaluation Form to the User Office.

Deadlines for submission of Experimental Reports

- 1st March for experiments carried out up until June of the previous year;
- 1st September for experiments carried out up until January of the same year.

Instructions for preparing your Report

- fill in a separate form for each project or series of measurements.
- type your report, in English.
- include the reference number of the proposal to which the report refers.
- make sure that the text, tables and figures fit into the space available.
- if your work is published or is in press, you may prefer to paste in the abstract, and add full reference details. If the abstract is in a language other than English, please include an English translation.

**Experiment title:**

Fluid-mobile element partitioning during serpentine formation and breakdown. New insights into the element recycling in subduction zones.

Experiment number:**ES-494**

Beamline: BM23	Date of experiment: from: 21/11/2016 to: 28/11/2016	Date of report: 10/9/2016
Shifts: 18	Local contact(s): Angelika D. Rosa	<i>Received at ESRF:</i>

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Report:

Serpentinites forming in subduction zone environments present a major sink for fluid-mobile elements at depth [1-2]. **Ni-enriched serpentines forming in laterites from the alteration of ultramafic rocks in turn can retain much more than 30 % of NiO, presenting Nickel-ore deposits of great importance for industry [3].** Because of the experimental challenges, which include the low elemental concentrations and the generation of high P/T conditions, our knowledge on how these elements are absorbed, transported and released at depth, during the formation and stepwise breakdown of serpentine is mainly based on field observations and ex-situ fluid inclusion studies [4,5]. We have therefore conducted experiments on the EXAFS beamline BM23 of the ESRF to study the serpentine formation and breakdown in a resistively heated diamond anvil cell.

In a first step, we tracked *in-situ* the absorption and release of Ni during serpentine involved reactions. We chose Ni because it is after Fe the second most enriched element in serpentine minerals [2], allowing us to characterize and optimize the experimental setup. For the experiment, the X-ray beam was tuned to the energy of the Ni K-edge (8.339 keV) using a double-crystal fixed exit monochromator equipped with two Si(111) crystals. Beam focusing to $6 \times 6 \mu\text{m}^2$ and harmonic rejection was achieved through a Kirkpatrick Baez mirror system with Pt coating. EXAFS and XRF measurements were conducted in fluorescence mode using a Si SDD Vortex detector in backscattering geometry (**Figure 1**). We used external and internally heated diamond anvil cells equipped with one full single-crystal diamond on the transmission side and one fully perforated single-crystal diamond sealed with a nano-crystaline diamond window on the backscattering side. XRF, XANES and EXAFS data were acquired at different P/T points to track the Ni-fluid concentration and the formation of new solid phases.

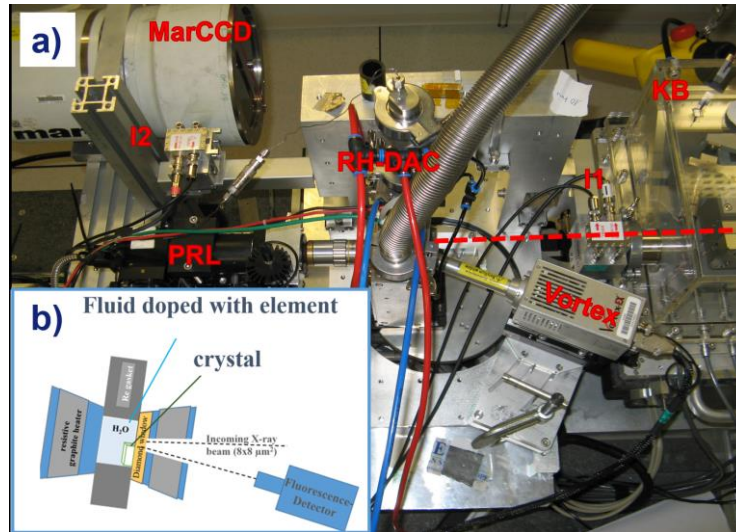


Figure 1. A) Top view of the experimental setup at BM23 developed for this study and B) diamond anvil cell geometry for the monitoring of low Z-elements.

- 1) For the formation reaction of serpentine we loaded a synthetic crystal of forsterite (Mg_2SiO_4) together with a ruby crystal and a NiCl_2 solution containing 0.5 m NaCl and 2500 ppm Ni and pressurized to 0.3 GPa. Nickel speciation in the fluid was then tracked from XAS measurements (Figure 2).

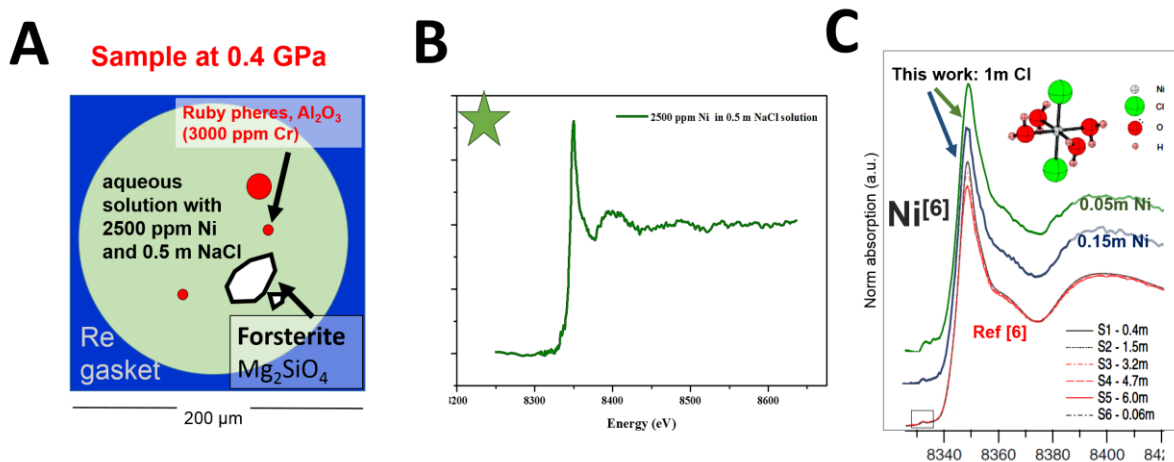


Figure 2. A) Schematic view of sample loading. B) Ni-EXAFS fluorescence spectra obtained in the fluid at 0.3 GPa. C) Comparison of Ni-XANES spectra obtained in this experiment in fluids doped with different concentrations of Ni and at different pressure (green 0.05m Ni at 0.3 GPa, blue 0.15m Ni, < 0.1 GPa) further compared to existing data at lower pressure (red, 0.04 GPa) [6].

The sample pressure and temperature was then raised to 0.3 GPa and a 300 °C using an externally heated diamond anvil cell for more than 12 hours. Serpentine formation reaction kinetics are very sluggish in nature but are enhanced by Al from one week to 36 hours [5]. We could observe very fast absorption of Ni from the fluid already after one hour after P/T stabilization by the newly formed serpentine. Nickel was then completely absorbed from the fluid after 3 hours (Figure 3).

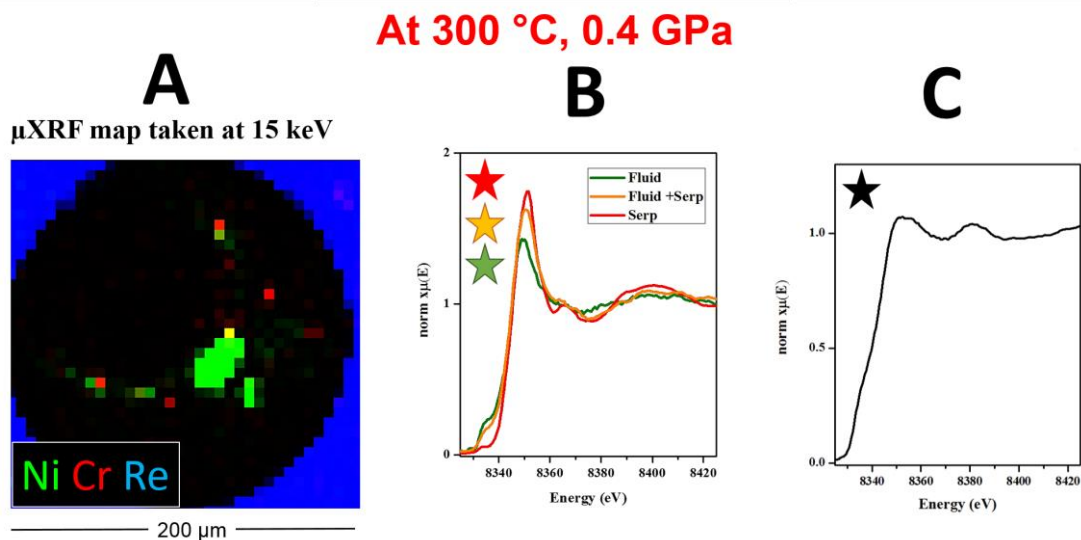


Figure 3. **A)** XRF map taken at 15 keV and during the serpentine formation reaction at 300 °C and 0.3 GPa. **B)** Serpentine XANES spectra taken at different steps of the reaction (green in the fluid at 0.3 GPa and ambient T , yellow at the onset of the reaction and red after the complete absorption of Ni). **C)** Ni XANES spectra obtained close to the ruby position indicating the formation of metallic Ni at this position.

Few amounts of Ni^0 form close to ruby spheres at 25 °C and 0.4 GPa (Figure 3 C). Ni^0 forms also during the reaction at 300 °C and 0.4 GPa. Ni^0 formation on the ruby is related to oxidation of Cr^{3+} to Cr^{6+} , triggered by the differences in redox potentials between Ni and Cr. This is an interesting result, showing that the addition of ruby in the sample chamber has influence on the redox buffering. During the reaction XRD images were taken evidencing the formation of Ni-serpentine (Figure 4). The XRD data will be then combined with high-quality EXAFS spectra obtained from the newly formed serpentine to better constrain the incorporation mechanism of Ni (Figure 5).

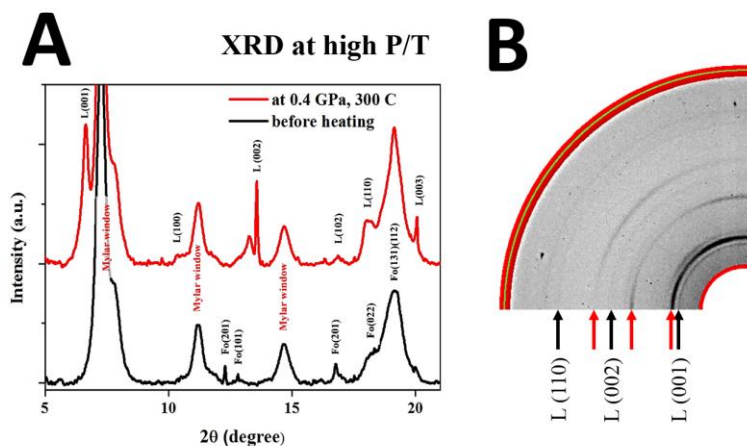


Figure 4. **A)** Integrated XRD images taken at ambient T (black) and high P/t conditions (red) at the position of the forsterite crystal (Figure 2). **B)** Raw XRD images taken during reaction showing the formation of Ni-serpentine peaks having powder like almost continues Debye diffraction rings which indicates that Ni-serpentine is finely grained slightly textured.

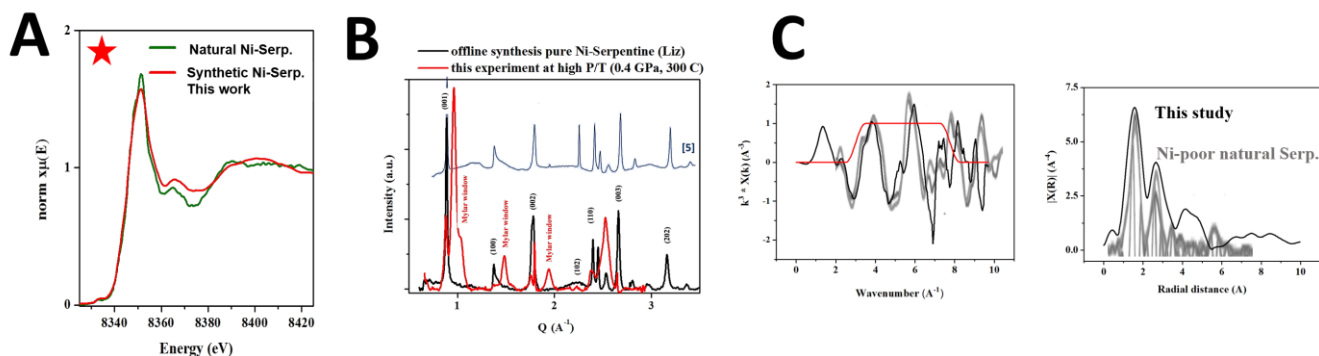


Figure 5. **A)** Comparison of Ni-XANES spectra of natural serpentine (green) and the one synthesized in the present study. **B)** Comparison of XRD images taken of Ni-enriched serpentine at ambient T (black and high P/T) as well as Ni-free serpentine synthesized in a similar manner as in the present work by [5]. Comparison of EXAFS analysis from Ni-serpentine (black, this study) and natural (grey, [6]).

- 2) For the breakdown of serpentine a synthetic Ni-serpentine with 2.5 wt% of Ni was loaded together with a 0.5 NaCl solution in an internally heated DAC. XAS spectra in the solid phase were acquired up to 1100 °C and 4.4 GPa. **We could observe the sequence of breakdown reaction of serpentine to forsterite and enstatite and finally the breakdown of enstatite to forsterite (Figure 2). We could however not observe any fluid signature in the XANES spectra suggesting that Ni is entirely transferred to the solid phases during serpentine breakdown.**

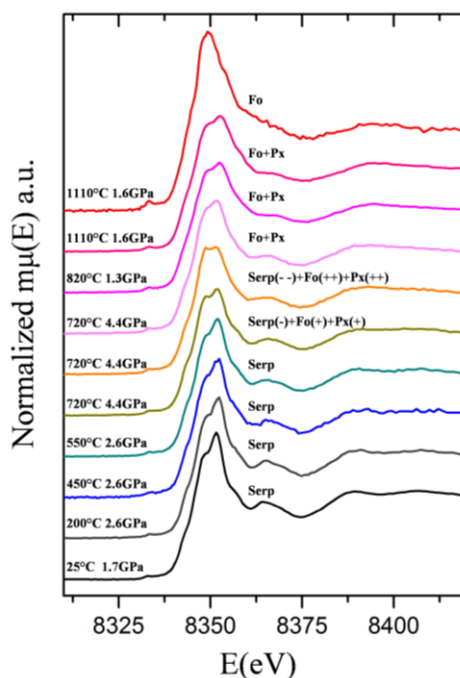


Figure 5. Normalized and merged Ni K-edge XANES acquired during the subsequent phase transitions. Liz, lizardite; Atg Antigorite; Ol, olivine; Py, pyroxene.

Results

1. Experimental setup

The setup used in the experiments, including the diamond anvil design and the measurement geometry was especially developed for experiments on low Z and low concentration elements in resistively heated diamond anvil cells (see report ES-370). The present experiments have shown that this setup can be used on fluid samples up to more than 1100 °C and 4.4 GPa and for EXAFS measurements down to concentrations of 1000 ppm. Recently we have been able to combine also an online Raman

system to this setup for further fluid characterization.

2. Ni behavior during serpentine involved reactions

We successfully conducted serpentine formation and breakdown experiments tracking the concentration of Ni in the fluid phases and newly formed solid phases. The acquired data are of high quality and are unique since they present the first in-situ data on this topic. We have found an extreme high absorption potential of newly formed serpentine for Ni from a fluid phase, indicating that Ni might be most likely mobilized in lateritic ore deposits and transported over a very short distance until serpentine forms. By comparison of XRD, EXAFS and XANES data from the synthetic and natural samples we will be able to understand better the incorporation mechanism of Ni in Ni-enriched serpentine deposits. Nickel contained in Serpentine subducted via slabs in turn might not be mobilized during its breakdown in the released fluid rather than being subducted further by anhydrous phases. Detailed data analysis is in progress and results are foreseen to be published in a high profile international journal this year.

Reference: [1] Deschamps et al., 2011, *Terra Nova*, 23, 171-178. [2] Deschamps et al., 2012, *Chem. Geol.*, 312-313, 93-117. [3] Suárez et al., 2008, *Macla* 10, 142-144 [4] Scambelluri et al., 2004, *Int. Geol. Rev.*, 46, 7. [5] Andreani et al., 2013, *Am. Min.* 98, 1738-1744. [6] Tian et al., 2012; *Chem Geology*, 334, 345-363.