



**Experiment title:** Arsenic transfers by the fluid phase in subduction zones: insights from *in situ* X-ray absorption spectroscopy in the diamond-anvil cell.

**Experiment number:**  
30-02-935

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**Names and affiliations of applicants** (\* indicates experimentalists):

- \* Carmen Sanchez-Valle, ETH, Zurich, Switzerland
- \* Gleb S. Pokrovski, LMTG –UMR 5563 of CNRS, Toulouse, France
- \* Jacques Roux, IPGP, Paris, France
- \* Olivier Proux, OSUG, CNRS, Grenoble, France
- \* Jean-Louis Hazemann, Institut Néel, ESRF, Grenoble, France

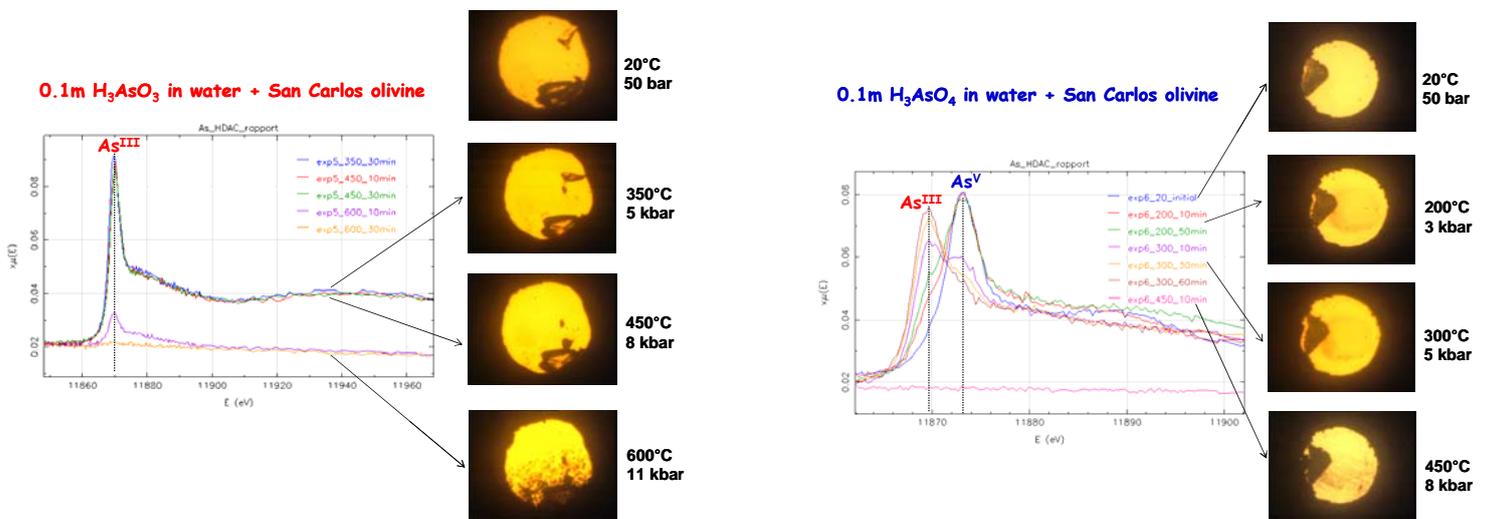
**Experimental strategy and setup:** The ultimate goal of this projet is to provide new data on arsenic speciation and behavior in the fluid phase pertinent to subduction-zone settings, in order to better quantify the geochemical cycles of volatile elements and develop new geochemical tracers of subduction-zone processes taking place on Earth. The present pilot experiment was intended to develop reliable tools allowing *in situ* measurement of As speciation, redox state and concentrations in aqueous solution at temperatures and pressures typical of conditions of the fluid generation in subduction zones ( $T = 20\text{--}600^\circ\text{C}$ ,  $P = \text{up to } 10\text{--}15 \text{ kbar}$ ). We used a modified Basset-type hydrothermal diamond-anvil cell (HDAC) equipped with a Re gasket and two heating resistances around the sample chamber [1,2]. Pressure in the cell was estimated from the *PVT* properties of pure water and assuming isochoric behavior of the compression chamber. Fluorescence spectra were recorded using a mono-element VORTEX detector placed at  $15\pm 2^\circ$  relative to the incoming beam. Visual changes in the sample space during measurements were monitored with a digital camera placed at  $55^\circ$  from the incoming beam. During the experiment, the cell was rotated around its vertical axis to allow spectra acquisition and imagery alternatively. The cell was constantly flushed with a 2% $\text{H}_2$ -98%Ar gas mixture to protect the heating elements, diamonds and seats from oxydation.  $\text{As}^{\text{III}}$  and  $\text{As}^{\text{V}}$ -bearing solutions (0.2 and 0.4 mol/kg, respectively) were prepared by dissolution of  $\text{As}_2\text{O}_3$  and  $\text{As}_2\text{O}_5$  solids in pure water followed by filtering through a 0.45  $\mu\text{m}$  Millipore filter. They were stored in tight Pyrex bottles and diluted with  $\text{H}_2\text{O}$  just before the experiment. In total, 7 experiments were performed starting with 0.1m ( $\sim 7000 \text{ ppm As}$ ) solutions of arsenious ( $\text{H}_3\text{AsO}_3$ ) or arsenic ( $\text{H}_3\text{AsO}_4$ ) acid with or without an olivine crystal (San Carlos, 10% of  $\text{Fe}^{\text{II}}$ ), which is a reference model material for the mantle wedge composition in subduction zones.

**Feasability tests:** To the best of our knowledge, we have been able to obtain, for the first time, exploitable XANES spectra from  $< 0.1\text{m As}$  aqueous solutions in a diamond anvil-cell in a wide  $T$  and  $P$  range. Rotation of cell within  $\pm 2^\circ$  allows getting rid of Bragg's peaks arising from the diamond windows in the XANES region of interest ( $-50$  to  $300\text{--}500 \text{ eV}$ ). The collected XANES spectra (Fig. 1) could be reliably treated in terms of identification of major spectral features, *in situ* monitoring of redox changes, and quantitative linear combination fit (LCF) analyses of  $\text{As}^{\text{III}}$  vs  $\text{As}^{\text{V}}$  fractions in the fluid phase. It was found that X-ray beam may induce redox changes both on  $\text{As}^{\text{III}}$  and  $\text{As}^{\text{V}}$  solutions upon prolonged exposure. Consequently, care was taken to minimize the cell exposure to the beam, particularly during alignments. However, other factors (e.g., Re gasket material) may also contribute to As chemical transformations (see below). Raman spectroscopy measurements will allow better decoupling these two factors.

**Results from the  $\text{As}^{\text{III}}$  system:** In experiments starting with arsenious acid ( $\text{H}_3\text{AsO}_3$ ,  $\text{pH}\sim 5$ ), it was found that this As form is stable up to at least  $650^\circ\text{C}$  and 15 kbar within the time of measurements (a few hours at a given  $T$ ), and exhibits spectra identical to those of  $\text{As}(\text{OH})_3(\text{aq})$  investigated recently at  $T \leq 500^\circ\text{C}$  and  $P \leq 600 \text{ bar}$  [3,4]. At the highest  $T$  investigated, the decrease of the fluorescence signal indicates minor losses of dissolved  $\text{As}^{\text{III}}$  from solution, likely due to its incorporation/alloying in the Re gasket. This important finding will guide our choice of more chemically inert materials, like Au or Pt, for future experiments. In the presence of olivine,  $\text{As}(\text{OH})_3$  is the major form in solution at moderate  $T$  ( $\leq 450^\circ\text{C}$ ), when the olivine dissolution is relatively weak. In contrast, at higher  $T$  with the rapid increase of olivine dissolution/alteration, As is almost completely lost from solution (Fig. 1), and is likely to concentrate in the solid phase as arsenites [ $\text{AsO}_3$ ]. This is in line with the available thermodynamics of  $\text{As}^{\text{III}}$  and  $\text{As}^{\text{V}}$  species and solid phases [5], which shows that  $\text{As}^{\text{V}}$  is not stable in the system fluid-olivine. This result has interesting

geological applications; it disagrees with the report, using XAFS spectroscopy, of most As in pentavalent form in subduction-zone serpentinites produced by interactions of the mantle wedge with fluids liberated from subducted sedimentary rocks [6]. We will attempt to re-measure As in these natural As-rich (~10-300 ppm) serpentinites samples by XAFS (coll. S. Guillot, LGCA, Grenoble; A. Arai, Kanazawa, Japan).

**Results from the As<sup>V</sup> system:** Arsenic acid solutions (H<sub>3</sub>AsO<sub>4</sub>, pH~2) are unstable in the present cell environment (and also under the beam), rapidly reducing to As<sup>III</sup> above 100°C. The instability of As<sup>V</sup> in solution disagrees with thermodynamic predictions which show that a 0.1 m H<sub>3</sub>AsO<sub>4</sub> solution is stable to at least 600°C. In contrast, in the presence of Re metal, thermodynamic calculations demonstrate that As<sup>V</sup> is reduced to As<sup>III</sup>, according to the reaction: H<sub>3</sub>AsO<sub>4</sub> + 0.5 Re = H<sub>3</sub>AsO<sub>3</sub> + 0.5 ReO<sub>2</sub>. This reaction is thermodynamically favorable in the whole *T-P* range, yielding As<sup>V</sup>/As<sup>III</sup> equilibrium ratios in solution less than 10<sup>-6</sup>. Thus, more inert gasket materials (Au, Pt) will be used to pursue this study. In the presence of olivine, the As<sup>V</sup> reduction is somewhat slower than in pure water, but does go to completeness at 300°C in 1 hour (Fig. 1 right). This slowness in comparison to olivine-free experiments might be related to less acidic pH induced by the olivine alteration, which stabilize anionic As<sup>V</sup> species. The effect of pH on As<sup>V</sup> reduction will be tested next time. The generated As<sup>III</sup> is rapidly lost from solution, like in experiments with As<sup>III</sup> (see above). Thus, olivine alteration products (e.g., serpentinite, magnetite) seem to efficiently scavenge As from the fluid phase, in agreement with natural observations (e.g., [6]).



**Fig.1.** Evolution of As K-edge XANES spectra as a function of time (in min) at indicated *T* and *P* for 0.1m As<sup>III</sup> (left) and As<sup>V</sup> (right) solutions in the presence of olivine in the diamond-anvil cell. These experiments demonstrate that *i*) As<sup>III</sup> is the stable redox state of arsenic at these conditions; *ii*) As<sup>III</sup> is efficiently scavenged from solution by olivine alteration products at  $T \geq 450^\circ\text{C}$ .

**Conclusions and perspectives:** This first exploratory experiment demonstrated the feasibility of in situ studies of both As speciation in high *T-P* solution and fluid-mineral interactions at conditions directly relevant to terrestrial subduction zone settings. Olivine alteration by aqueous fluids at 400-600°C results in efficient scavenging of As from the fluid and its incorporation in the solid products. The next step will be to investigate in situ in detail dissolved As behavior during fluid interactions with the major mantle silicate minerals (olivine, pyroxene, serpentinites) in the temperature range 300-600°C, as a function of pressure and solution pH, and to better characterize the alteration products and the chemical and structural status of As in the solid phase. A far improved cell design with chemically inert materials (Au, Pt), more accurate pressure measurements (from diffraction patterns of internal sensors, Au), and focused X-ray beam will be used in the next XAFS experiment. It will be complemented by Raman spectroscopy measurements in the same model fluid-mineral systems, and by studies of As-rich natural samples in order to provide a self-consistent picture of the As fate in subduction zone processes.

**References:** [1] Bassett et al. (1993) Rev. Sci. Instrum. 64 (8), 2340-2348 [2] Sanchez-Valle et al. (2004) J. Phys. Cond. Matter 16, S1197-S1206; [3] Pokrovski G.S. et al. (2002) Geochim. Cosmochim. Acta 66, 3453-3480; [4] Testemale D., Hazemann J.L., Pokrovski G.S. et al. (2004) J. Chem. Phys. 121, 8973-8982; [5] Perfetti E., Pokrovski G.S. et al. (2008) Geochim. Cosmochim. Acta 72, 713-731; [6] Hattori K.H. et al. (2005) Geochim. Cosmochim. Acta 69, 5585-5596.