	Experiment title: In situ XAS study of arsenic behavior in a fluid-mantle rock system: applications for the development of new geochemical tracers of subduction-zone dynamics	**Experiment number**: EC-755

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Report:

Experimental strategy, setup and limitations: The goal of this experiment was to provide first data on arsenic chemical speciation and behavior in fluid-mineral systems of subduction-zone settings on Earth, for better quantifying the geochemical cycle of this element and developing new geochemical tracers of subduction-zone processes. In this experiment, As^{III} and As^{V}-bearing aqueous solutions were reacted with olivine and serpentine+magnetite. These minerals are the major constituents, respectively, of the pristine mantle-wedge rocks (peridotite) and metamorphic rocks formed by fluid-peridotite reactions. Thus, our model systems directly reflect the conditions of subduction zones and allow in situ measurement, using X-ray absorption spectroscopy, of As speciation, redox state and concentration in aqueous solution and minerals up to 600°C and 30 kbar. We used a modified Basset-type hydrothermal diamond-anvil cell (HDAC) [1,2] equipped with a rhenium gasket coated with gold, which provides a chemically inert environment and avoids reactions of the sample with the container at elevated *T*. Pressure in the cell was measured using the diffraction pattern of metallic gold. The X-ray beam was focused to ~30×30 μm using KB mirrors. The small beam size compared to the cell diameter (~200 μm) allows probing As spatial distribution between fluid and minerals. Based on our previous experiments, care was taken to minimize beam exposure of the sample to avoid radiation-induced redox changes common for this element. Fluorescence spectra at As K-edge were recorded using a mono-element detector placed at 20±1°, with the cell at 10±1°, relative to the outgoing beam. Visual changes were monitored with a microscope placed at 30° from the incoming beam. The cell was constantly flushed with a $5\%H_2$-$95\%Ar$ gas mixture to protect the heating elements, diamonds and seats from oxidation. As^{III} and As^{V}-bearing solutions were prepared by dissolution of As_2O_3 and As_2O_5 solids in pure water or NaOH. In total, 7 experiments were performed starting with 0.15 mol/kg (~10000 ppm As) solutions of arsenious (H_3AsO_3) or arsenic (H_3AsO_4) acid with/without olivine ($Mg_{1.8}Fe_{0.2}SiO_4$, 10% of Fe^{II} from San Carlos peridotite) or antigorite+magnetite ($Mg_3Si_2O_5(OH)_4$+Fe_3O_4, from Himalayan serpentinites). The high As concentrations are dictated by the necessity to obtain a exploitable fluorescence signal from a focused beam in a diamond-anvil cell. Although our experimental concentrations and As(aq)/mineral ratios are much higher that those encountered in natural systems, they nevertheless allow the major trends of As behavior to be obtained for the first time from in situ measurements at subduction zone conditions.

Results from the As^{III} system. Arsenious acid bearing solutions (pH~5) were found to be stable to at least 600°C and 30 kbar in our cell configuration. The amplitude of the As fluorescence signal both in mineral-free and mineral-bearing systems generally decreases with increasing *T*, likely reflecting both the decrease of *P* (density) and the reduction of the sample volume that can be excited with the microbeam. At a given *T*, the signal from solution without minerals remains constant with time (to at least 3h), demonstrating that neither precipitation nor reaction with the cell material occur. XANES spectra from solutions without minerals are similar, with some minor differences, to those of As(OH)₃ at lower *T-P* [3,4,5].

In the presence of olivine, from 20 to 300°C no change in As^{III} concentration or redox state occurs in the fluid. At 450°C, As^{III} reduction and concentration (×3-5 of signal intensity compared to the fluid) is observed on the olivine and its alteration products, while As(OH)$_3$(aq) remains the dominant form in the fluid. At 600°C, the difference between As contents in the olivine and fluid attains a factor of 10 (in terms of signal intensity) in favor of the solid phase (Fig. 1). The chemical status of precipitated As is likely to be iron arsenides (FeAs, FeAs$_2$) and/or native As, as indicated by comparison with spectra of reference compounds (Fig. 1). As^{III} is not detectable (< 10% of total As) in the solid phase, demonstrating that As^{III} sorption on the olivine or its alteration products is minor at these conditions. Thus the major reaction controlling arsenic scavenging from the fluid phase upon interaction with the mantle peridotite is likely to be:

Fe$_{0.2}$Mg$_{1.8}$SiO$_{4(olivine)}$ + As(OH)$_{3(aq)}$ + H$_2$O ↔ Mg$_3$Si$_2$O$_5$(OH)$_{4(antigorite)}$ + Fe$_3$O$_{4(magnetite)}$ + FeAs$_{2(lollengite)}$. This is in agreement with thermodynamic predictions of olivine hydrolysis from 300 to 600°C showing the formation of iron arsenides, antigorite and magnetite as the main phases (± brucite and talc, depending on T-P).

In the presence of the antigorite-magnetite assemblage from 20 to 450°C, the As^{III} fluorescence signal exhibits a similar decrease with T as for mineral-free solutions, and shows no As enrichment in any part of the cell. XANES spectra at spots both from solution and antigorite are similar to As(OH)$_3$. At 600°C, however, As was found to be partially reduced (likely As^0 or Fe-arsenides) and enriched by a factor of 2-3 in the proximity to antigorite, as compared with the fluid where As(OH)$_3$ remains largely dominant. Thermodynamic calculations in the system As^{III}(aq) + pure Mg antigorite + magnetite show that As(OH)$_3$ is stable in solution and that no reduced As-bearing phase could form. Therefore, the observed reduction and precipitation of As in the proximity of the minerals might be due to the presence of minor amounts of pristine olivine or other Fe(II)-bearing silicates like Fe-antigorite whose reaction with water leads to Fe^{II} oxidation and As^{III} reduction, in agreement with the equilibrium thermodynamic calculations in the olivine-water system above. The relatively large beam-size delivered by FAME did not allowed accurate measurement of As spatial distribution and identification of neo-formed minerals at the μm scale.

Results from the As^V system. An arsenic acid-bearing solution (0.15m H$_3$As^{V}O$_4$-0.2m NaOH, pH~6) is reduced to As^{III}(OH)$_3$ at 300°C during ~1 h (80% of total As) without any change in total dissolved As concentration (Fig. 1). Although this reduction is much slower than in our previous experiments with Re gaskets, it is prohibited thermodynamically in the chemically inert environment of an Au-coated cell. In fact the reduction of As^V to As^{III} by water would require values of the Gibbs free energy of arsenic acid and its anions 150-200 kJ/mol (!) higher (i.e., less negative) than those available. This is inconceivable with the existing thermodynamic data for As-bearing species [6]. Consequently, this reduction is very likely to be induced by the X-ray beam, similar to findings at lower pressures [4]. 'Less destructive' in situ techniques like Raman spectroscopy are necessary to fully resolve this issue.

In the presence of the antigorite-magnetite assemblage, As^V reduction to As^{III} is complete within less than 1 min. upon attainment of 300°C. The dissolved As^{III} concentrations remained stable for at least 2 hrs. Such fast reduction, in comparison to the mineral-free solution above is unlikely to be beam-induced, but is due to the presence of magnetite that controls the redox potential in the system. This is in quantitative agreement with thermodynamic calculations, indicating the formation of the antigorite-magnetite-hematite assemblage and As(OH)$_3$ in the fluid phase at this temperature. Fast and complete As^V reduction to As^{III} in solution was also observed in previous experiments with olivine. Thus our experiments demonstrate that As^V is not stable either in solution or solid phase in the fluid-mineral systems of subduction zones.

Geological applications and perspectives: This first in situ study of As in fluid-mineral systems typical of subduction zones demonstrates that 1) As^{III}(OH)$_3$ is the major As aqueous form in the fluid phase at conditions of peridotite hydrolysis and serpentinite formation; 2) As^{III} may be efficiently scavenged from the fluid phase during olivine hydrolysis leading to formation of insoluble iron arsenides and/or native arsenic; the presence of Fe^{II} in the silicate minerals (olivine and antigorite) is the key condition for As^{III} reduction and precipitation; 3) sorption/incorporation of As^{III} into minerals is expected to be minor compared with scavenging via arsenide formation; 4) As^V is not stable in the fluid-mineral systems investigated over the whole T-P range.

These findings are in agreement with thermodynamic predictions using available data. They imply that the major part of As coming from the sediments and sea water into subduction zones should be scavenged at moderate temperatures (< 450°C) in the form of sulfide and arsenide minerals under highly

reduced conditions of olivine hydrolysis, then transported along the slab, and finally partly liberated in the form of As[III] into the fluid phase upon serpentinite dehydration and sulfide/arsenide oxidation at higher T. As a result, this redox-sensitive trace element may be a very useful tracer of redox conditions and dynamics of subduction zones. For example, the finding of dominant fractions of As^{5+} together with more reduced As forms (As^{3+} and As^{n-}) in Himalayan serpentinites exhumed from a depth of 100 km [7] indicates that these samples are likely to have undergone As oxidation during their long travel to and/or stay at the Earth surface. Thus in situ analyses of As redox and chemical forms in mantle minerals may allow identification of post-formational changes that may also affect the interpretation of the signatures of many other elements.

In situ spectroscopic techniques in the diamond anvil-cell open large perspectives for studying water-rock interactions and element distribution in deep geological processes. The present work will be complemented by Raman spectroscopy measurements in model systems allowing better identification of the neo-formed minerals and avoiding radiation-induced damage. XAS and Raman data in model laboratory systems, coupled with analyses of As-bearing natural samples, will provide a self-consistent picture of the fate of arsenic in subduction zone processes.

References:
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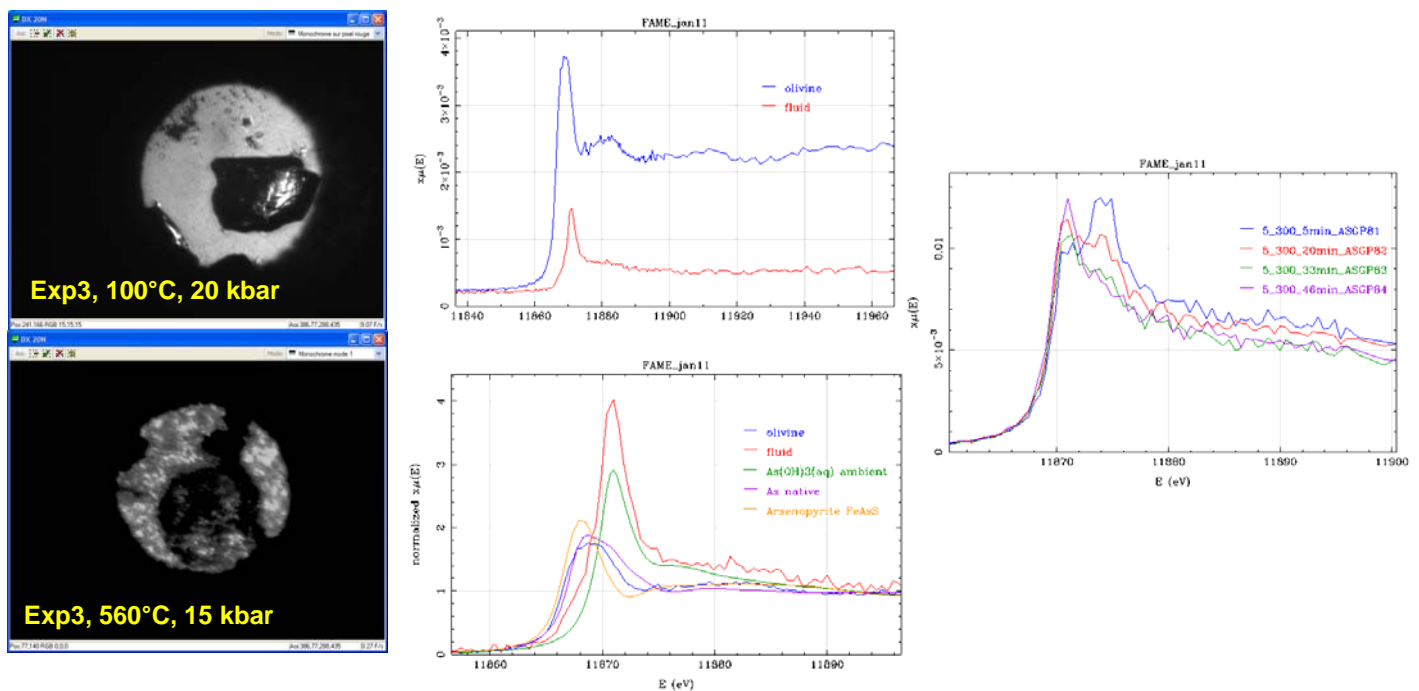
Fig.1. *Left*: HDAC images in an experiment in the olivine-fluid system at indicated T and P. Note changes in the olivine crystal at high T due to alteration.
Center: Raw and normalized XANES spectra from the fluid phase and altered olivine at 560°C and their comparison with reference compounds. Note the predominance of reduced As on the olivine, likely in the form of native As or arsenide, and the enhancement of the white line of As(OH)$_3$ in comparison to ambient conditions, which might ne due to changes in molecular symmetry at elevated T-P [e.g., 5].
Right: XANES spectra from an arsenic acid solution (pH~6) at indicated time after the attainment of 300°C showing relatively slow As^{V} oxidation to As^{III} in solution under the beam exposure.