ESRF	**Experiment title: GeO_2 solubility and Ge diffusion in aqueous fluids at high pressure and temperature by synchrotron X ray fluorescence (SXRF)**	**Experiment number**: HS-2256
Beamline: ID22	**Date of experiment**: from: 27/11/03 to: 2/12/03	**Date of report**: *Received at ESRF:*
Shifts: 15	**Local contact(s)**: Alexandre Simionovici	

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Report:

During the allocated beam time in ID22 (experiment HS-2256), we have follow the dissolution of GeO_2-rutile in KBr salt solutions (0.01 and 0.1 m) up to 400 ºC and 6.10 GPa in an externally heated diamond anvil cell (DAC) using Synchrotron X-ray fluorescence spectroscopy (SXRF). The concentration of Ge in the fluid at various P-T conditions was determined using the known concentration of Br^- as an internal calibrant, following the protocol described in [1].

We have used an incident monochromatic X-ray beam of 16 keV focused with an achromatic Kirkpatrick-Baez (KB) Rh coating mirror to exciting the fluorescence of the sample. This experimental setup ensures a spatial resolution of 2x7 ?m^2 and a flux of 9.10^{10} photons per second. The intensity of the incident and transmitted beam was monitored by silicon PIN-diodes located before and after the sample. X-ray fluorescence was collected using an energy dispersive solid state Si(Li) detector (150 eV resolution and 12.5 mm^2 active area) set at 30° from the incoming beam. This high collection angle was achieved using the specially modified DAC for fluorescence experiments described in Ref. [2]. Within this experimental configuration, the detection limit (DL) for Br in the fluid is about 36 ppm. The compression chambers were formed from 80-?m thick platinum-lined stainless steel foils drilled with two separate holes (Fig.1): a large one (?125-150 ?m) loaded with several pieces of compacted GeO_2-rutile powder (grain size ? 10 ?m) in the KBr solution aqueous solution for solubility measurements, and a second one (?75 ?m) loaded with a ruby chip imbibed in paraffin for pressure calibration. The isolation of the ruby pressure gauge is required by the high chemical reactivity of the fluid, resulting in the completely dissolution of the sensor up to 300 ºC (report HS-2099).

When the DAC was vertically positioned in the beam, the high density of the GeO_2-rutile (6.52 $g.cm^{-3}$) produced the precipitation of the sample at the bottom of the cell, forming a planar solid/fluid interface (Fig. 1). The X-ray fluorescence analyzes carried out at different points in the fluid reveal the existence of vertical Ge concentration gradients in the fluid. In order to obtain the diffusion coefficient for Ge in the aqueous fluid at different pressures and temperatures, we have measured Ge diffusion profiles through the sample chamber.

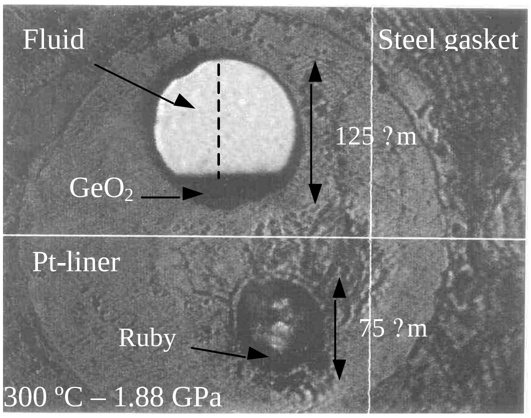

Fig.1. Photograph showing the compression chamber arrangement used for GeO_2-rutile dissolution experiments and diffusion measurements. The dashed line shows the path followed for sampling the fluid.

The location of the solid/fluid interface was determined by scanning vertically the sample chamber for the K? energies of Ge and Br (Fig.2).

X-ray fluorescence analyses were then undertaken in order to determine the Ge concentration in both halves of the interface. Spectra were recorded with an exposure time of 300 seconds per point at incremental distances of 5 to 10 ?m from the top to the bottom of the cell, following the path indicated in Fig.1. As an example, the Ge diffusion profile measured in the compression chamber at 300 ºC and 1.88 GPa is reported in Fig.3.

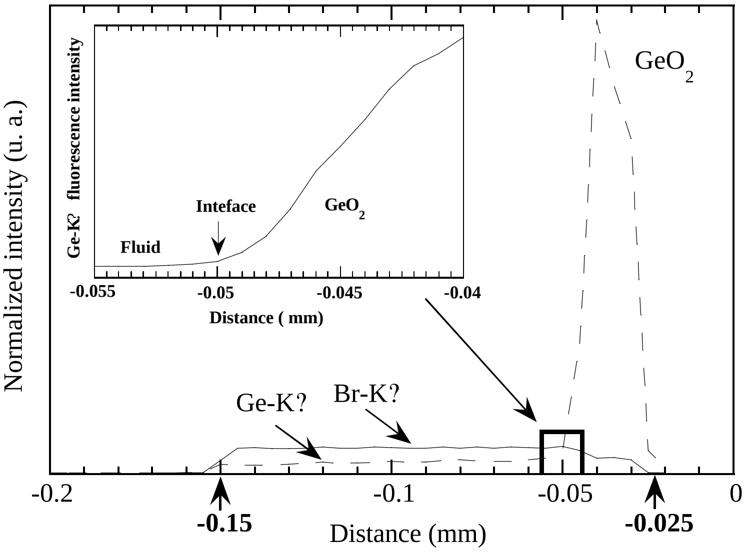

Fig.2. Vertical fluorescence scan for Ge and Br through the sample chamber at 300 ºC and 1,88 GPa. The inset shows the Ge fluorescence profile recorded to accurately determine the position of the solid/fluid interface.

The evaluation of the diffusion coefficients of Ge in high P-T aqueous fluids is currently in progress. In spite of this, the preliminary results presented here show the suitability of the SXRF technique for the *in situ* study of elemental diffusion in aqueous systems under high P-T conditions. These data are essential for the modeling of diffusive transport of elements and its influence on the growth and dissolution of minerals. In the following months, we expect to prepare a manuscript about the solubility of GeO_2-rutile and the diffusive transport of Ge in high P-T aqueous fluids.

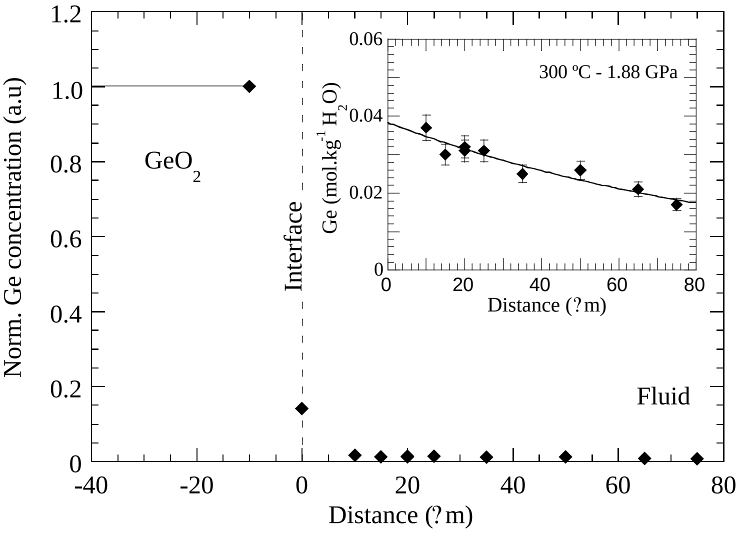

Fig.3. Ge diffusion profile at 300ºC and 1.88 GPa. Ge concentration is normalized by the value measured in the solid. The distance is measured relatively to the solid/fluid interface. The inset shows the details of the distance-dependent Ge concentration in the fluid.

References

[1] Sanchez-Valle et al. 2003. Dissolution of strontianite at high P-T conditions: An *in situ* synchrotron X-ray fluorescence study. *American Mineralogist*, 88, 978-985.

[2] Sanchez-Valle et al. 2003. Progress in quantitative analysis of high P-T fluids using SXRF. Sous presse in *Journal of Physics: Condensed matter*.