ESRF	**Experiment title: In-situ XAFS investigations of transition elements in hydrous silicate melt at high temperature and pressure**	**Experiment number**: ME 836
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Shifts: 15	**Local contact(s)**: Alexandre Simionovici	*Received at ESRF:*

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Report:

Silicate melts and aqueous fluids play a major role in the evolution of the Earth's crust and mantle. Melt generation and subsequent ascent are major geologic processes in the evolution of the Earth's crust, also leading to abundant volcanic activities on the surface of the earth. The dissolution of volatiles such as water, which is strongly pressure-dependant, leads to considerable changes in physical and chemical properties of these melts. During rapid ascent of such melt bodies, exsolution of the dissolved volatiles is often considered to be one main factor for hazardous, explosive volcanic eruptions. Knowledge of physical and chemical properties of the materials of these systems is essential for a better understanding and modeling of the processes involved. 3d-transition elements such as Iron (Fe), rare earth elements and natural actinides (Th/U) are often used to determine the geological history and genesis of magmatic rocks. Structural studies of the speciation of these elements in such systems are important for a correct interpretation and modeling of data collected in natural systems.

We have collected XANES spectra at high temperature and high pressure using a hydrothermal diamond-anvil cell to characterize the structural state of Fe, U and Th in hydrous silicate melts at in-situ conditions equivalent to the deeper earth's crust. The XANES spectra were collected at the Fe K-edge and at the U/Th L_3-edge using the Si (111) double-crystal monochromator. The beam was focussed at the experiment down to a spotsize of 4.5 x 6 µm using the KB-mirror optics. Element contents in the samples ranged between 1000 ppm (U, Th) and 1 wt% (Fe, U, Th). The spectra were acquired in fluorescence mode collecting the fluorescence yield in 90° to the incoming beam using a Si(Li) solid state detector (for details of the setup see Schmidt & Rickers 2003). Maximum temperature and pressure achieved were 700°C and 1 GPa, respectively.

Fe: The XANES spectrum taken on the water-saturated melt at 700°C and 500 MPa indicates that the local structure around Fe^{2+} is quite similar to the one found in anhydrous melts of similar composition. After lowering of the temperature of 50°C a narrowing of the "white line" and additional features after the main crest are observed that indicate onset of crystallization in the sample. Similar features were observed in spectra taken on samples quenched from similar conditions (Wilke et al. 2002a,b). Based on these in-situ measurements, it is now evident that the local structure around Fe in hydrous glasses may be substantially affected by the quench process and that the structure found in such glasses is not representative for the melt above the temperature of glass transformation.

U/Th: XANES spectra taken on U indicate the presence of U(IV) due to the reducing intrinsic conditions in the cell. A comparison to a spectrum taken at room temperature after the run does not reveal any differences. For NS3, hydrous melt and aqueous fluid turn into a homogeneous fluid above 460°C. This, however, has no influence on the observed spectra. Observation made for Th are quite similar. In the U-bearing haplogranitic composition, however, U quickly precipitates as UO_2 in the melt. This result is consistent with earlier synthesis attempts using an albitic composition (Na_2O-Al_2O_3-$3SiO_2$) also with 1 wt.% U) under reduced oxygen fugacity conditions, which resulted in the nucleation of UO_2 (Farges et al., 1992).

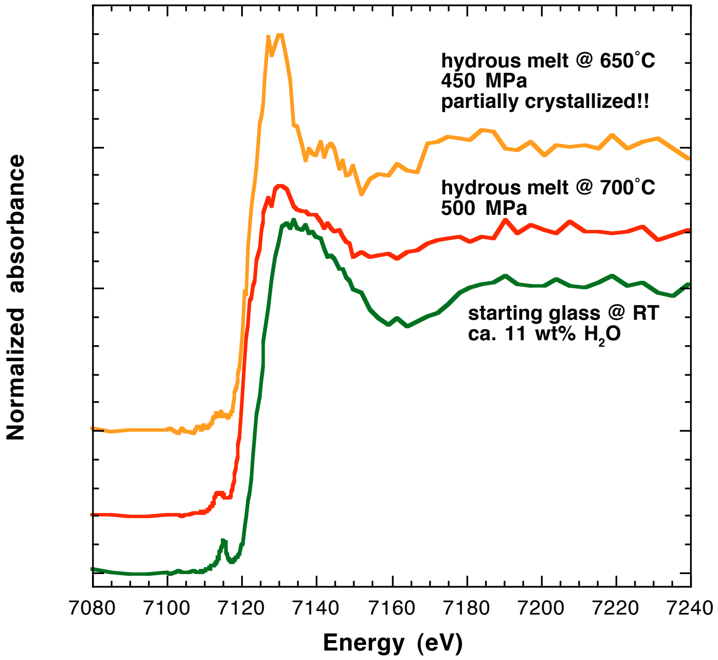

Fig. 1: XANES spectra of Fe in hydrous haplogranitic silicate melt at the conditions indicated. Spectrum taken on the glass refers to the starting glass pre-saturated with water. Starting glass and melt differ in the Fe oxidation-state due to the difference in intrinsic redox conditions of the synthesis and the in-situ run.

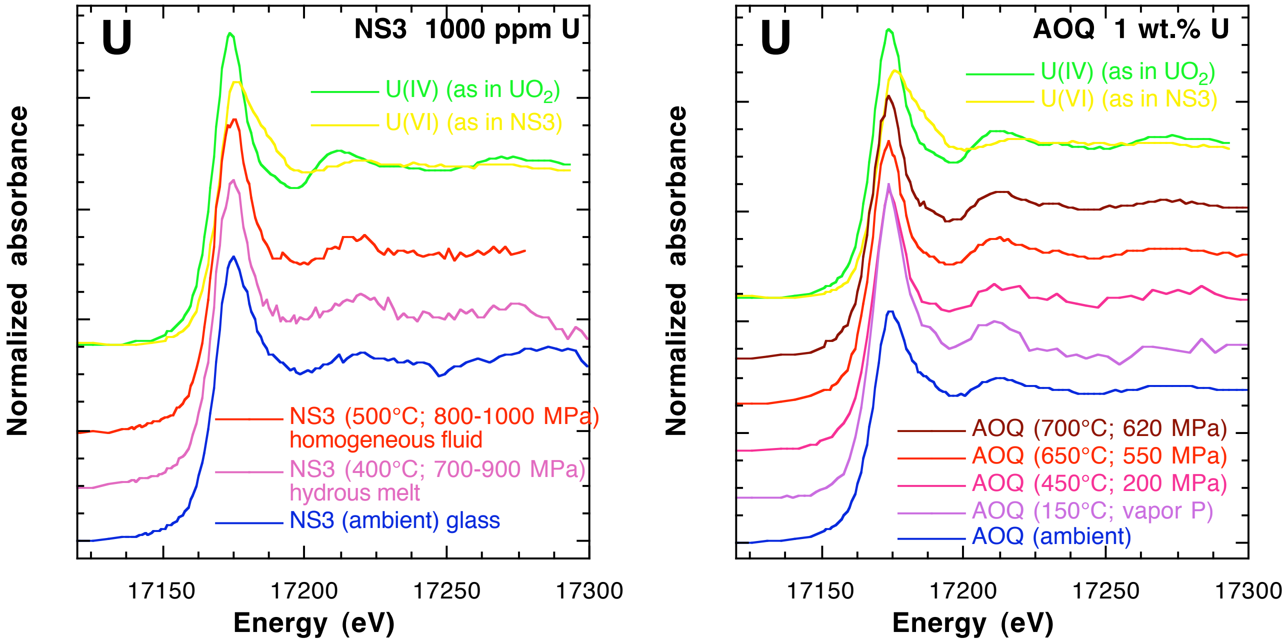

Fig. 2: XANES spectra of U in hydrous sodium trisilicate (NS3) and haplogranitic (AOQ) melt and glass (after run) at the conditions indicated.

References:

Farges F., Ponader C.W., Calas G. et Brown G.E., Jr. (1992) *Geochim. Cosmochim. Acta,* 56, 4205-4220.
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