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At ID22 beamline, we performed XAFS spectroscopy with a KB micro-focused beam. We collected spectra on a large dozen of U- and Th-Bearing Ca-perovskites with different starting materials and different synthesis conditions. Those samples were previously synthesized and quenched using a multi-anvil press (MAP) at the Laboratoire Magmas et Volcans (Clermont-Ferrand).

The spectra were resolved enough in eV to provide a good redox information about the uranium in each sample. We can tell on first sight of μ -XANES that uranium exclusively adopts a 4+ oxidation state in Ca-perovskite (Fig 1.). We performed 2D mapping in several areas of the samples revealing unexpected uranium and thorium heterogeneities (Fig. 2). Additional spectra were collected in heterogeneous zone of the U-Ca-perovskite we could locate on the map. We did not find any evidence of the presence of hexavalent U^{6+} in the U-bearing Ca-pv. The same method of analysis was performed on all samples, testing different starting material and different U-Ca-Pv synthesis conditions, then we only observed the U^{4+} oxidation state in all samples.

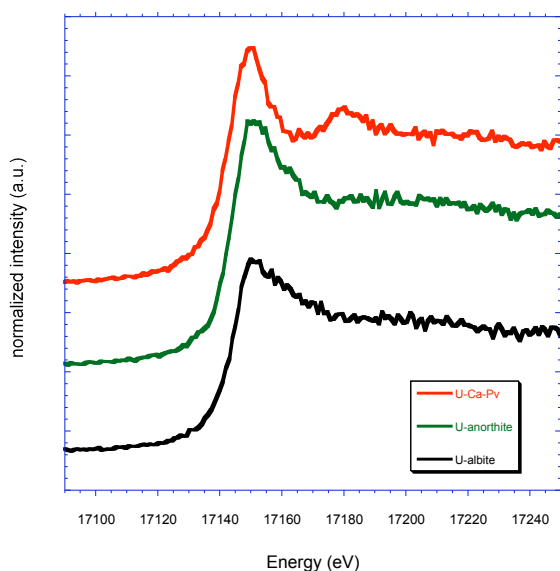


Fig. 1: example of Uranium μ -XANES collected for U-bearing Ca-perovskite, U-anorthite as a standard for U^{4+} and U-albite as a standard for U^{6+} (data is under processing).

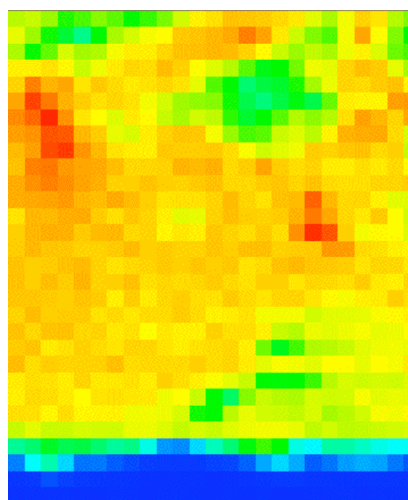


Fig. 2: 2D $U-L_{\alpha}$ mapping of uranium in a quenched U-bearing Ca-pv synthesized in multi-anvil cell apparatus. Red zones are U-rich (U-Ca-Pv heterogeneities), and blue are the uranium-less zones (Platinum around the sample)

We collected μ -XANES spectra of Th-bearing Ca-perovskite as a model for tetravalent U. Th occurs only in a 4+ oxidation state and Th^{4+} presents ionic radius and electronic properties comparable to U^{4+} . The spectra we obtained display great similarities with U-bearing Ca-pv and (U,Th)-bearing Ca-pv.

The resolution of the spectra is enough to confirm the expected oxidation state of uranium. But we obviously do not have the EXAFS resolution necessary to determine the full speciation of U and Th in our samples. Nevertheless, the resolution of the first EXAFS oscillations seems to be enough to extract the coordination number of both U and Th in their related Ca-perovskite phases.

We tried to make additional *in situ* and ambient measurements on a synthesized U-bearing Ca-perovskite at 30 GPa. We used a “Le Toullec” diamond anvil cell (DAC) provided by the “sample environment” laboratory. The cell was loaded by cryogeny at ID27’s laboratory. The sample was a thin oxide powder plate loaded in the DAC, with argon as the transmitting pressure medium. We performed two sided anneals at high temperature (2000-2500K during 15 minutes) by using the ID9 laser facility. Measurements were done with the DAC in both transmission and fluorescence count mode. We observed that U^{4+} is the only oxidation state of uranium in the Ca-perovskite. Then both HP-HT techniques (DAC and MAP) gives the same oxidation state for uranium, e.g; U^{4+} (see figure 3), indicating rather reducing conditions;

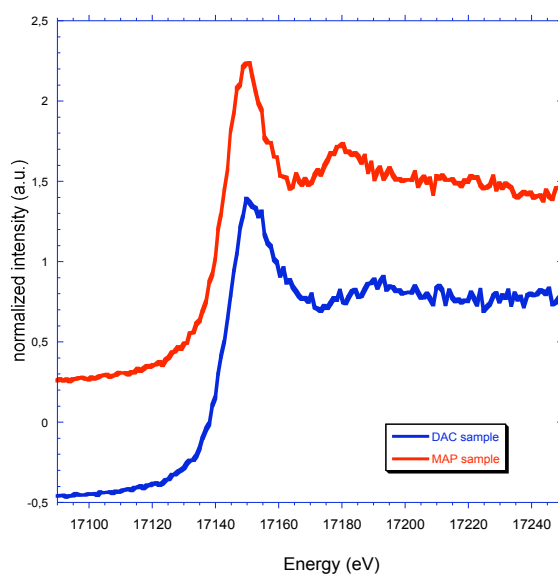


Fig. 3: example of Uranium μ -XANES collected for U-bearing Ca-perovskite in DAC sample and in quenched MAP sample.

At the present time, we are reducing the data to determine the local coordination of uranium, thorium. The presence of U and Th in nano-domains with another valence for U (+6, +5, +3...) needs to be considered. The uranium and thorium environments in the Ca-perovskite are not yet determined, but are different from an eight-fold cube predicted for the uranium and the thorium in UO_2 and ThO_2 . This indicate that a full incorporation of U and Th in the Ca-perovskite structure is more expected than eventual AO_2 nano-clusters (with $\text{A} = \text{U}$ and/or Th), but this need to be confirmed.