



	Experiment title: Structural characterization of natural actinides (Th and U) in radiation damaged ceramics and analogues	Experiment number: CH-768
Beamline: ID26	Date of experiment: from: 02/11/1999 to: 09/11/1999	Date of report: 29/09/2000
Shifts: 8	Local contact(s): Pierre Emmanuel PETIT	<i>Received at ESRF:</i>
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Report:

We studied several natural zircon (ZrSiO_4) samples with variable degrees of radiation damage. These minerals are considered as natural analogues for industrial ceramics. These last materials will be used to store high-activity nuclear wastes in the close future (Chakoumakos et al., 1987, Ewing et al., 1987, Weber, 1990, Hess et al., 1998). Industrial ceramics for nuclear wastes and natural analogues have both accumulated α -doses greater than 10^{18} α /mg. The first are damaged because of their high current radioactivity over short period of time (Pu, Cs, Np, Am, etc...). The latter are damaged because of their great age (10^9 years). So, they are comparable in terms of received doses to the ceramics containing high-activity actinides. We designate by "metamict", any crystalline mineral that lost their crystallinity due to radioactive damage. In order to help understanding radioactive waste materials, we are studying the local structure around Th and U in these natural mineral analogues of high-activity ceramics.

The samples were previously characterized using x-ray diffraction, electronic microprobe analyses and SEM/TEM imaging. In natural samples, the U and Th contents is low (1000 – 100 ppm). It is thus necessary to use a method sensitive to short-range order around ultra diluted cations, such as x-ray absorption spectroscopy (XAS) on an undulator beamline. Such method has been extensively used to determine the disorder effect in minerals (Brown et al., 1988). In addition, the ID26 beamline is suitable to collect high quality XAS spectra in these extreme conditions. In 1999, we had beam time (8 shifts) to collect XANES and EXAFS data at the Th and U L_{III} edges on these samples and at 30 K and room temperature.

Thorium L_{III} edge

Until now, we studied the local environment around Th in several zircon samples (titanite, CaTiSiO_5 , and monazite, CaCePO_4 , are still under investigation). We have studied in details the differences in the local structure around Th in crystalline and metamict zircon. In crystalline zircon, it is well known that Th substitute for Zr (ionic radius with 20%: Goldschmidt's rules). However, the substitute mechanism at the \AA scale is still unknown (like most substitution process in minerals). These XAFS methods are well suited to study these aspects.

The crystalline zircon, originally metamict from Naegy, Japan, was annealed at 1200°C for 3 hours. It serves as a model for the original sites of Th before metamictization. We checked with x-ray diffraction and Zr-K EXAFS (data collected at LURE) data that this sample is fully crystalline.

In crystalline zircon, the oxygen first neighbors around Th are at an average inter-atomic distance similar to that measured in crystalline thorite (α -ThSiO₄): 2.41(5) Å (Taylor and Ewing, 1978). This EXAFS-derived average distance is consistent with eight-fold coordinated Th. Therefore, this short-range environment is not in agreement with a simple ionic substitution mechanism. In contrast, it is more consistent with a ZrO₈-ThO₈ substitution mechanism. Similarly, we measured Th-Si pairs at 3.16(5) and 3.90(5) Å, as observed in crystalline thorite (Taylor and Ewing, 1978). These results are also in sharp contrast to those measured in crystalline zircon (2.99(5) and 3.64(5) Å: Hazen and Finger, 1979). In contrast, we have detected Zr 4th neighbors around Th.

The EXAFS-derived Th-Zr distance (3.74(5) Å) is closer to the Zr-Zr distance in zircon (3.64(5) Å) than the Th-Th distance in thorite (3.90(5) Å). Calculations on inter-cations angles (example: $\widehat{\text{Th-O-Zr}} = 109^\circ$) confirm that Zr 4th neighbors are in an intermediate local structure between zircon-like thorite-like environment (angle $\widehat{\text{Zr-O-Zr}} = 111^\circ$ and angle $\widehat{\text{Th-O-Th}} = 107^\circ$). Above 4 Å around the Th central atom, oxygen 5th and 6th neighbors are observed at a distance similar to that measured around Zr in crystalline zircon. Therefore, the local structure around Th in crystalline zircon is similar to that of thorite up to 3.90(5) Å around the central Th. That is only above this distance, that a local structure related to zircon is observed (Zr 4th neighbors). So, the substitution mechanism of Th in crystalline zircon suggests considering, not just a simple ionic replacement mechanism, but instead, a larger structural unit, i.e., ThO₈Si₂Si₄ moieties to replace ZrO₈Si₂Si₄ within the zircon structure. Such large structural expansion (within 4 Å around the central Th) must be at the origin of defects in the crystal structure of such crystalline zircon.

Then, we also studied a metamict zircon to determine the effect of radiation damage on this mineral. We have found that the local structure around Th (including 4th neighbors) is not similar to that observed in crystalline zircon. All atoms around Th are located at a distance similar to that measured in crystalline thorite. In contrast to Th in crystalline zircon, no Zr 4th neighbors are detected at 3.70(5) Å. Instead, Th neighbors are measured at 3.90(5) Å. The Th-Si inter-atomic distance at 3.20(5) Å is similar to that in crystalline zircon 3.16(5) Å (within errors).

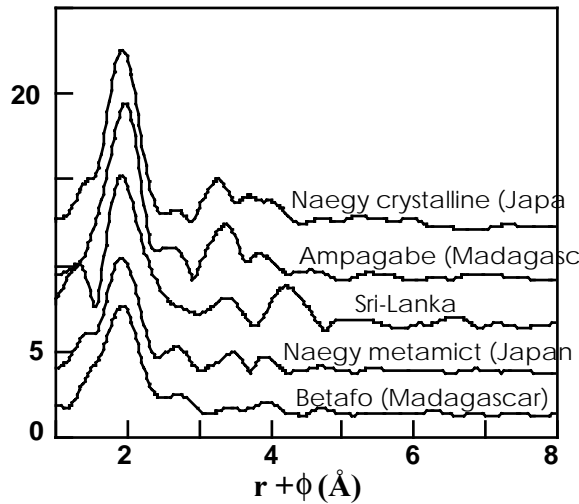


Fig. 1 – Fourier Transform of several zircons showing differences between crystalline and metamict zircons.

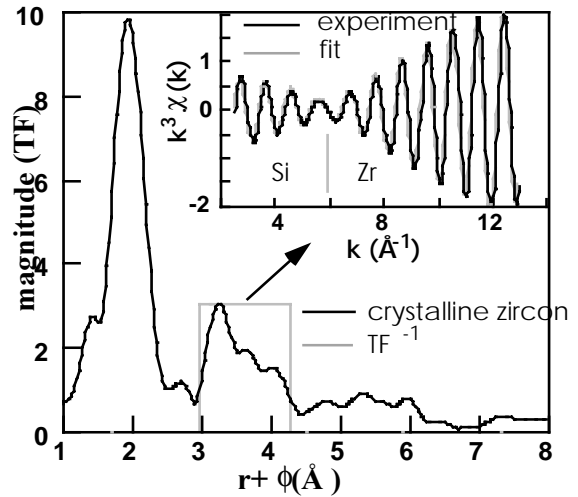


Fig. 2 – Fourier Transform of the crystalline zircon and the fit of Si and Zr next nearest neighbors, assigned to Th-Si and Th-Zr pairs in a thorite-like cluster

We have also studied several radiation-damaged zircons from different locations. The local environment around Th changes from one sample to another. It varies from a structure completely metamict (ex: metamict zircon from Naegy, Japan), to almost crystalline (ex: crystalline zircon from Naegy, Japan). Preliminary results are reported in table 1.

Table 1. XAFS results for some zircon samples.

Sample origin	Th-O			Th-Si			Th-Si			Th-Th or Th-Zr		
	N	R	σ^2	N	R	σ^2	N	R	σ^2	N	R	σ^2
* Crystalline zircon, Naegy.	8	2.40	0.009	1	3.16	0.01	3	3.90	0.01	3	3.74	0.005
										(Zr)	(Zr)	(Zr)
* Metamict zircon, Naegy.	9	2.42	0.010	1	3.20	0.01	4	3.90	0.01	4	3.90	0.050
										(Th)	(Th)	(Th)
* Sri-Lanka	9	2.42	0.008	2	3.17	0.02	4	3.70	0.05	2	3.65	0.010
										(Zr)	(Zr)	(Zr)
* Ampagabe, Madagascar.	10	2.42	0.005	1	3.16	0.01	4	3.90	-0.03	3	3.90	0.001
										(Th)	(Th)	(Th)
* Betafo, Madagascar	9	2.42	0.005	1	3.16	0.04	4	3.90	0.01	5	3.9	-0.009
										(Th)	(Th)	(Th)

Uranium L_{III} edge

The U-L_{III} edge is energetically located at 17166 eV but Y-K edge is only 128 eV before. The fluorescence yields for Y-K and U-L_{III} edges, are about 0.65 and 0.5, respectively. So, XAS spectra at U-L_{III} edge are in most cases affected by the EXAFS of Y. However, electron microprobe analyses of several natural metamict zircon samples showed that U in zircon is most abundant than Y. Indeed, some samples show a U/Y ratio of 10. The measured Y-K and U-L_{III} edges do not show this predicted trend. Therefore, we are strongly questioning electron microprobe analyses performed for U in these samples. Then, we are currently undertaking PIXE (Particle Induced X-ray Emission) experiments (CEA, Saclay) to measure these trace element concentrations more accurately. Also, we could not unfortunately use an energy discriminant fluorescence detector, which is known to minimize the effect of Y (Lomenech et al., 2000).

However, the XANES data collected at the U-L_{III} edge are good enough to derive important redox information. Some edges (crystalline zircon from Naegy, Japan, zircons from USA and Madagascar) are shifted by 6 eV to higher values in energy, as compared to that of uraninite (UO₂) which is a model for U(IV). Such a shift in energy position is characteristic of the presence of U(VI). The XANES spectrum is also characteristic of the uranyl group, U(VI)O₂²⁺, (Fig.3) with axial and equatorial oxygen making distinct contributions to the XANES (Fig.4), in excellent agreement with polarized XANES experiments (Templeton and Templeton, 1982). Uranyl groups cannot partition easily onto the bulk zircon, so these meoities result from the oxidation of the original U(IV), probably related to the radiation damage and subsequent weathering. However, we are investigating the possibility for other forms of U(VI), like in UO₃

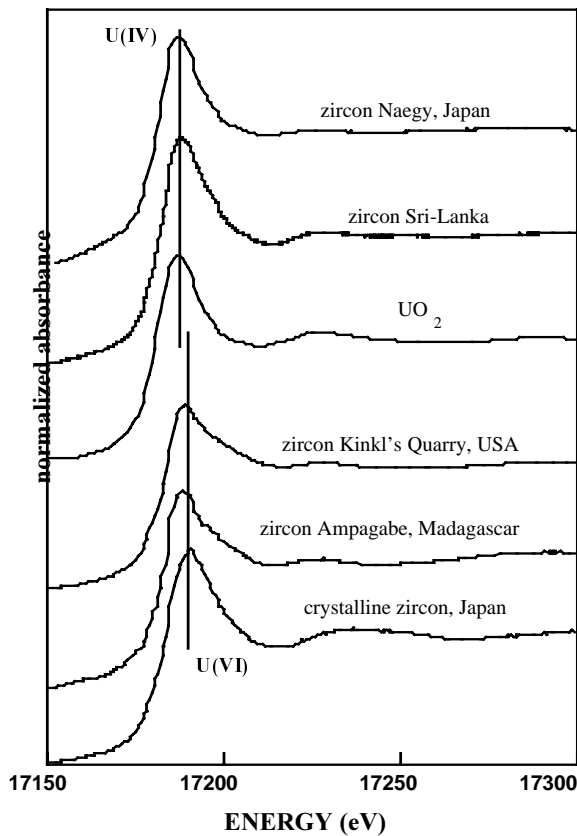


Fig. 3 – Experimental XANES spectra collected at U-L_{III} edge of some zircon samples compared to UO₂.

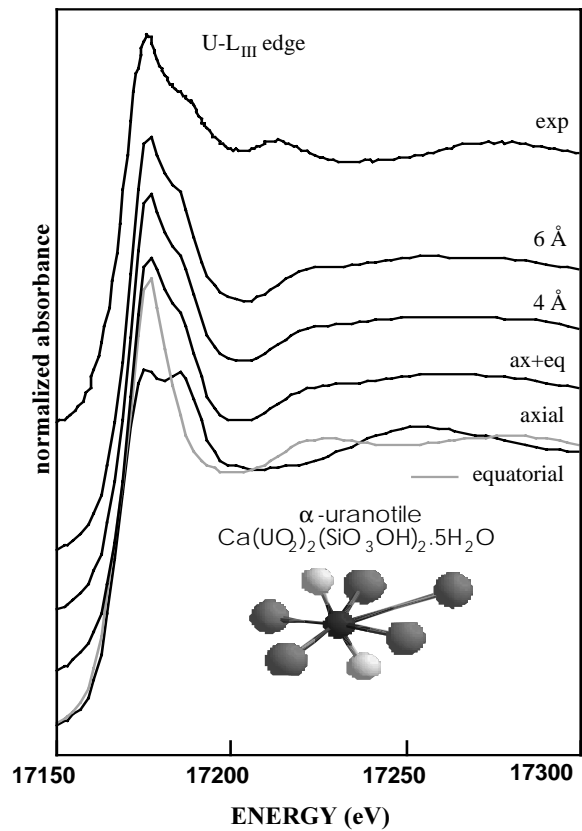


Fig. 4 – XANES calculation for different clusters around U in α -uranotile, as compared to an experimental XANES. Axial and equatorial represent oxygen first neighbors at short and long inter-atomic distance respectively.

Natural samples are used to study radiation damage in high-activity ceramics. They show the presence of U(IV) and U(VI). In spite of metamict state of some zircon (metamict zircon from Naegy, Japan, zircon from Sri-Lanka,...) no oxidation of U(IV) is detectable. Therefore, U in such material is stable as U(IV). Therefore, environment contamination risks in such metamict zircon are dismissed. However, other zircons show U(VI) which is much more soluble, so able to contaminate percolating water (and then the environment). We are working to better

understand these fundamental differences, by studying more samples using combined approaches, including molecular dynamics done at the CEA-Marcoule (by Delahaye and Ghaleb).

Aknowledgements.

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