Proposal CH-768 – 1999 Activity report

The project is untitled "Structural characterization of natural actinides (Th and U) in radiation damaged ceramics and analogues". We studied natural zircon ($ZrSiO_4$) samples with variable degrees of radiation damage (Table I). 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). Industrial ceramics and natural analogues have accumulated α-doses greater than 10^{18} α/mg. First because of their high current activity over short period of time ; because of their great age (10^9 years) for the latter. So, they are comparable, in terms of received doses, to the ceramics containing high-activity actinides (Np, Pu etc...). In order to resolve radioactive wastes stocking problem, we are close to study local structure around Th and U in these natural minerals.

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 such as x-ray absorption spectroscopy (XAS). Such method has been extensively used to determine the disorder effect in minerals (Brown et al., 1988) Therefore, the ID26 beamline is suitable to collect high quality XAS spectra.

The samples were previously characterized using X-ray diffraction, electronic microprobe and SEM/TEM imaging. 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 5 K.

Table – I Samples identification:

Origin of the sample	color	α-dose/mg (10^{16})	Radiation rate in (μs_v/h)	Age in (Ga)
Zircon ($ZrSiO_4$)				
Naegy, Japan	gray-green	2	1.1	0.125
Ampagabe, Madagascar	brown	3	1.0	0.5-1.65
Hitterö, Norway	white	2	0.9	0.9-1.64
Sri-Lanka (unknown location)	green	0.5	1.0	0.56
Kinkel's Quary (USA)	brown-black	6	5.4	0.3-0.35
Betafo, Madagascar	brown	3	0.5	0.5-1.65
Diamantina, Brazil	brown	-	0.1	-
Sri-Lanka	green	0.2	0.35	0.32-0.42
Titanite ($CaTiOSiO_4$)				
Tranomaro, Madagascar	gray-black	0.2	0.12	-
Khebina, URSS	brown	0.2	0.1	-
Kailboute, Madagascar	brown-white	0.2	0.1	-
Capelinha, Brazil	green	-	0.15	-
Monazite ($CaCePO_4$)				
MAOC		-	9.10	-
FG		0.2	2.45	-
Herfoss, Norway	brown	-	2.5	-
Marijao, Madagascar	yellow	-	2.65	-

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 change in the local structure around Th in crystalline and metamict zircon. We designate by metamict crystalline minerals that lose their crystal structure due to radioactive destruction.

The crystalline zircon, originally metamict, was annealed at 1200°C for 3 hours. It serves as a model for the original sites of Th before metamictization.

In crystalline zircon**,** the local structure around Th is with regard to the structure of a synthetic zircon (Hazen et Finger, 1976). The oxygen first neighbors around Th are at an average interatomic distance similar to that measured in crystalline thorite ($ThSiO_4$): 2.41 Å (Taylor et Ewing, 1978). EXAFS-derived eight-fold coordinated Th. Therefore, this short-range environment is in agreement with the proposed $Zr \leftrightarrow Th$ substitution mechanism. Similarly, we measured Th-Si pairs at 3.16 and at 3.9 Å as observed in crystalline thorite (Taylor et Ewing, 1978). These results are also in sharp contrast to these measured in crystalline zircon (2.99 and 3.64Å: Hazen et Finger, 1979). In contrast, we have detected Zr 4^{th} neighbors around Th. The EXAFS-derived Th-Zr distance (3.74Å) is closer to Zr-Zr distance in zircon (3.64 Å) than the Th-Th distance in thorite. Calculations on inter-cations angles (example: Th-O-Zr = 108°) confirm that Zr 4^{th} neighbors are in a local structure closer to that for zircon. Up to 4Å around Th, oxygen 5^{th} and 6^{th} 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 3.9 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., $ThO_8Si_2Si_4$ moieties. Such large structural expansion (within 4 Å around the central Th) must be at the origin of defects in the crystal structure of such 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 is similar to that observed in crystalline zircon. All atoms around the absorber have distances similar to those measured in crystalline thorite. In contrast of crystalline zircon, no Zr 4th neighbors are detected at 3.7 Å. Nevertheless, the number of neighbors is weakly higher than theoretical one. Inteatomic distance of Si second neighbors is 3.20 Å considered as higher than in crystalline zircon (3.16 Å).

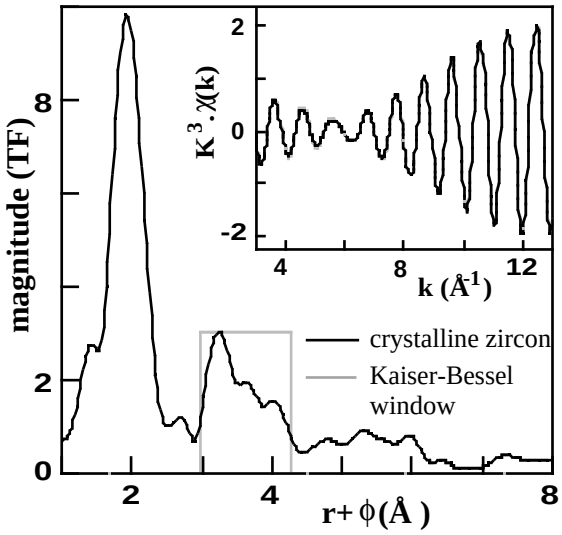

Fig. 1 – fit of Si and Zr, 3nd and 4th neighbors, in crystalline zircon reported to Th-Si and Th-Zr pairs of thorite cluster.

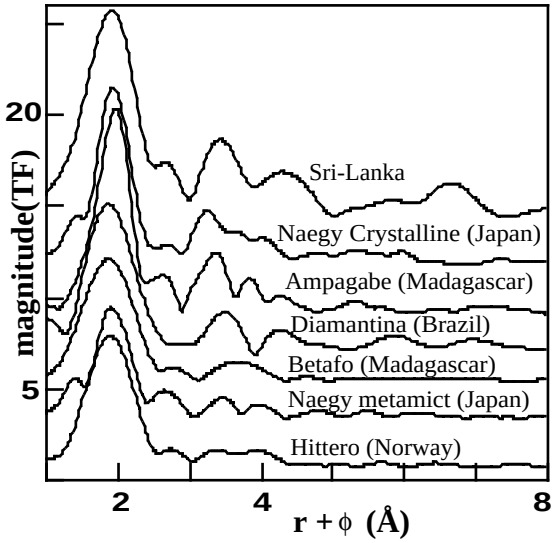

Fig . 2 – Fourier transform of several zircons shows difference between crystalline and metamict zircons we have studied.

We have also studied several radiation-damaged zircons from different locations. the local environment around Th change from one sample to another. It vary from structures completely metamict (ex : zircon Naegy, Japan), to almost crystalline (ex: zircon Sri-Lanka). Results are reported in next table II.

Table II :

Sample origin	Th-O			Th-Si			Th-Si			Th-Th		
	N	R	σ^2	N	R	σ^2	N	R	σ^2	N	R	σ^2
Crystalline zircon (Naegy)	7.73	2.4	0.009	0.6	3.16	0.008	3.35	3.93	0.01	2.6 (Zr)	3.74 (Zr)	0.005 (Zr)
Naegy metamict (Japan)	9.5	2.418	0.01	1.28	3.20	0.009	4.2	3.9	0.01	4.5	3.92	0.05
Srilanka	9.5	2.417	0.008	1.72	3.165	0.02	3.7	3.71	0.05	1.12 (Zr)	3.65 (Zr)	0.01 (Zr)
Ampagabe (Madagascar)	10.3	2.417	0.005	1.15	3.16	0.006	3.6	3.88	-0.03	2.4	3.9	0.0005
Betafo (Madagscar)	8.9	2.417	0.005	1.05	3.16	0.04	3.6	3.9	0.006	4.8	3.89	-0.009
Kinkel Quary (USA)	7.86	2.416	0.005	0.72	3.163	0.03	6.2	3.9	0.06	4.7	3.9	0.004
Hittero (Norway)	7.22	2.414	0.005	1.58	3.162	0.04	5.2	3.9	0.05	5.5	3.90	0.02
Diamantina (Brazil)	7.44	2.417	0.0008	0.7	3.16	0.03	4.3	3.9	0.01	4.15	3.9	0.02
Incertities	1.0	0.01	0.001	1.0	0.01	0.001	1.0	0.01	0.001	1.0	0.01	0.001

(Zr) represent a Th-Zr atomic pairs

Uranium L_{III} edge

We have collected data at the U-L_{III} edge. 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 (Table III). U-L_{III} edge is energetically located at 17166 eV and Y-K is only 128 eV before. Given Fluorescence yields for this two elements (0.5 for U and 0.65 for Y). So, XAS spectra of U collected at L_{III} edge are in most cases affected by the EXAFS of Y. We could not use an energy discriminant fluorescence detector, which is known to minimize this effect. We tested the possibility of the Y-K edge EXAFS signal to contaminate the U L_{III} edge EXAFS spectra. Based on model compounds calculations, we observed that atoms second and third neighbors are very influenced by Y-K. Figure 3 illustrate the influence of Y on disorder local around U. The U-L_{III} edge XAFS spectra show unfortunately that the K edge of Y is greater than that for U in all the samples studied. We believe that our previous electronic microprobe analysis underestimated the actual Y contents in our samples. Therefore, EXAFS spectra at U-L_{III} edge are usually highly influenced by the K edge of Y. The used of a energy-discriminant detector should minimize significantly the signal arising from Y, as recently observed at LURE on a study of the sorption of uranyl moieties on zircon. 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 Sri-Lanka) are shifted by 6 eV to higher values in energy, as compared to that of uraninit (UO_2) which is a model for U(IV). Such a shift in energy position is characteristic of the presence of U(VI). The XANES is characteristic of the uranyl group, UO_2^{2+} (see Fig. 4), which is a form of oxidized uranium. Uranyl groups cannot partition onto zircon and they therefore result from the oxidation of the original U(IV), probably related to the radiation damage and subsequent weathering.

Table III . Chemical analysis for some zircon

	Naegy, Japan	Ampagabe Madagascar	Hitterö, Norway	Sri-Lanka	Kinkel Quary USA
ZrO_2	53.90	56.75	64.30	63.75	49.55
SiO_2	27.80	19.80	32.53	32.15	25.90
P_2O_5	1.05	00.50	00.00	00.00	00.40
CaO	0.00	00.80	00.00	00.00	01.55
FeO	0.05	01.90	00.00	00.00	00.85
MnO	0.00	00.05	00.00	00.00	0055
Y_2O_3	1.65	00.80	00.00	00.25	00.85
Ta_2O_5	1.10	-	-	-	-
HfO_2	4.60	04.70	1.35	01.60	07.10
UO_2	4.70	01.85	00.30	00.20	05.60
ThO_2	2.85	01.35	00.05	00.05	00.05
PbO	0.05	00.20	00.05	00.10	00.10
H_2O	2.00	00.20	-	-	7.10

Notes:

- H_2O value is determined by the Penfield method (± 0.1)
- Experimental conditions for microprobe analyses: 15kV, 5 mA, spot size: 4 μm

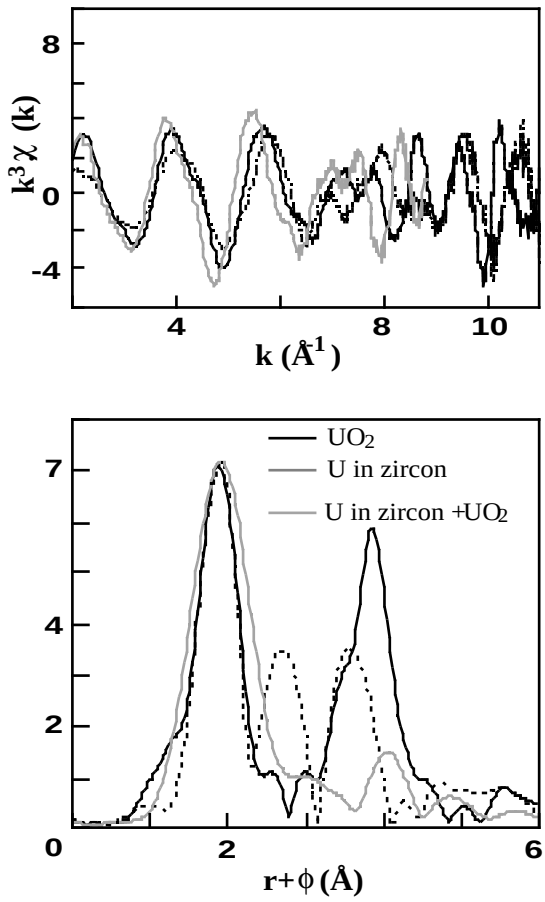

Fig. 3 – Fourier transform and $k^3.\chi(k)$ of U-L_{III} edge, showing the influence of Y-K edge EXAFS signal on the 2nd, 3rd , etc. neighbors around U.

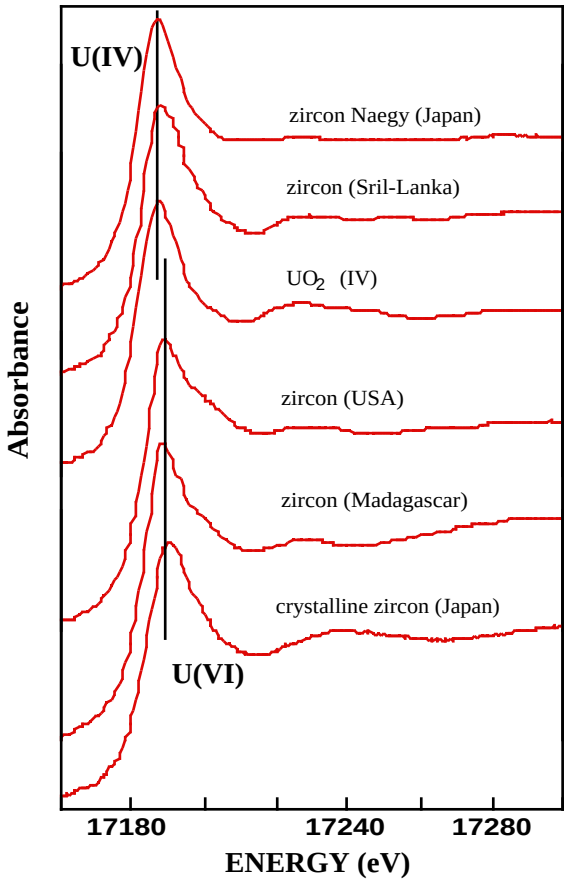

Fig. 4 – XANES spectra at U-L_{III} edge of some zircon samples compared to UO$_2$

In order to minimize the fluorescence due to Y, we tried to collect XAFS spectra at the U-L_{II} edge (20948 eV). In spite of the small intensity of this edge, we collected fair data. To have good spectra at U-L_{II} edge we should accumulate some spectrum.

Conclusion

We have found that local structure in metamict zircon around Th is almost nearer to that of crystalline one. This local structure is similar to the structure of crystalline thorite. Nevertheless, it is more extended in zircon metamict. Therefore, the thorite crystalline structure can replace crystalline zircon one by receiving α-recoil damage for a long time.

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