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# HVEM-TANDEM AND EELS STUDY OF RADIATION DAMAGE IN ZIRCONOLITE*

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# HVEM-TANDEM AND EELS STUDY OF RADIATION DAMAGE IN ZIRCONOLITE

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Zirconolite ($CaZrTi_2O_7$) is the major host phase for actinides in Synroc, a promising waste form for the immobilisation of high-level radioactive waste[1]. The effect of radiation damage on the structure and durability of zirconolite are important to predictive modelling of zirconolite's behaviour in the repository environment and risk assessment.

In this study, radiation damage effects in zirconolite were investigated by irradiating samples with 1.5 MeV $Kr^+$ ions using the HVEM-Tandem at Argonne National Laboratory (ANL) and energy loss electron spectroscopy (EELS). The HVEM-Tandem consists of a modified AEI high votage transmission electron microscope interfaced to to a 2 MV tandem ion accelerator. EELS spectra were collected using a Philips 420 TEM, operated at 120 kV, fitted with a Gatan Model 607 Serial EELS. EELS data were recorded at resolutions of ~1.0 eV and at a dispersion of about ~0.25 eV.

Selected area diffraction patterns (SADs) of individual grains of various zirconolites were monitored as a function of dose to establish the critical dose for amorphisation ($D_c$). A representative sequence is shown in Figure 1 and results for all samples are summarised in Table 1. We found that i) $D_c$(zirconolite) is independent of the atomic weight of dopants in zirconolite and the mean atomic weight of the sample and that ii) the Bragg reflections in SAD patterns which persist to the highest doses are firstly those resulting from the fluorite sublattice and secondly the four (110)-type reflections which lie on the innermost of the two diffuse rings representative of amorphous zirconolite. Within experimental error, our $D_c$(undoped zirconolite) value agrees with that measured by Ewing and Wang[2] ($4 \times 10^{14}$ ions $cm^{-2}$) and disagrees with that measured by White et al.[3] ($1 \times 10^{15}$ ions $cm^{-2}$). However on the basis of computer simulations of ion irradiation Smith et al.[4] suggest that White et al.'s $D_c$(undoped zirconolite) value may be high. Assuming this to be true, it may also explain why White et al.'s data suggested that $D_c$(zirconolite) depended on the atomic weight of dopant species, which is in contradiction to the trend we observed.

The Ti L edges of undoped zirconolite before and after ion irradiation, and two Ti standards ($TiO_2$ and $Ti_2O_3$) are shown in Figure 2. Comparison of the zirconolite and Ti-oxide spectra suggests that Ti predominantly exhibits a valence of 4+ in both unirradiated and irradiated zirconolite and that the bond lengths in zirconolite are similar to those in $TiO_2$. The electron energy loss near edge structure (ELNES) of the Ti L shell is consistent with the Ti changing from octahedral coordination to tetrahedral coordination[5]. As the irradiated material is amorphous at this point, analysis of the ELNES is one of the few ways that this change in the electronic structure can be determined at the local level. To quantitatively measure the changes due to irradiation, we fitted the zirconolite Ti-L spectra with four Lorentzians (in a similar manner to Morrison et al.[6]) and calculated $L_2/L_3$ and $L^*_2/L^*_3$ and $L_3 - L^*_3$ (Table 2). $L_2/L_3$ is the same before and after irradiation which suggests that radiation damage does not significantly affect the number of holes in the d-band (and hence valence). $L^*_2/L^*_3$ increases and $L_3 - L^*_3$ decreases after irradiation which suggests that radiation damage in zirconolite causes a distortion of the octahedral field around Ti atoms toward a tetrahedral configuration, consistant with previous X-ray absorption near edge structure and the extended x-ray absorption fine structure studies of natural zirconolite[7].

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8.)The authors thank the HVEM-Tandem Facility staff at ANL for assistance during ion irradiations and partial support by the U.S. DOE, Basic Energy Sciences, under contract W-31-109-ENG-38. The authors thank Peter Fielding (UNE), Lou Vance (ANSTO) and Alan Cuelho (UTS) for making and kindly providing the samples.

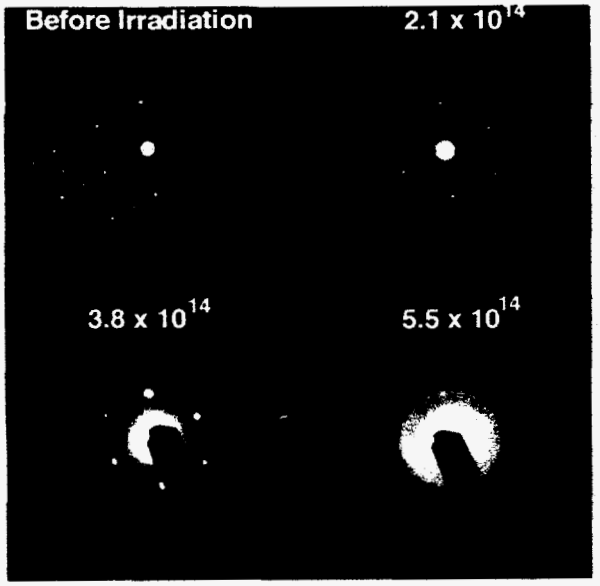


Figure 1. SADs of a zirconolite-2M grain viewed down [110] showing the effect of increasing dose. a) Before irradiation. After b) 0.85, c) 2.6, d) 3.0, e) 3.5, f) 4.7 x $10^{14}$ ions $cm^{-2}$.

| Material | Critical Dose (ions $cm^{-2}$) |
|---|---|
| Undoped Zirconolite - 2M<br>Mean At. No. = 14.6<br>$(Ca_{0.96}Zr_{0.01})_{0.97}Zr_{1.0}(Ti_{1.95}Zr_{0.05})_{2.0}O_{7.0}$ | 5.5 x $10^{14}$ |
| Nd + Zirconolite- 2M<br>Mean At. No. = 15.2<br>$(Ca_{0.81}Nd_{0.17})_{0.98}Zr_{0.97}(Ti_{1.89}Zr_{0.11})_{2.0}O_{7.0}$ | 5.3 x $10^{14}$ |
| Nd + Zirconolite - 3T<br>Mean At. No. = 15.3<br>$(Ca_{0.77}Nd_{0.19})_{0.96}Zr_{0.97}(Ti_{1.89}Zr_{0.11})_{2.0}O_{7.0}$ | 3.9 x $10^{14}$ |
| U + Zirconolite - 2M<br>Mean At. No. = 14.9<br>$(Ca_{0.88}U_{0.08})_{0.96}(Zr_{0.99}U_{0.01})_{1.0}(Ti_{1.76}Al_{0.23}Zn_{0.01})_{2.0}O_{7.0}$ | 3.8 x $10^{14}$ |
| Th - Zirconolite 3T<br>Mean At. No. = 16.5<br>$(Ca_{0.82}Th_{0.10})_{0.92}(Zr_{0.89}Th_{0.11})_{1.0}(Ti_{1.52}Zr_{0.48})_{2.0}O_{7.0}$ | 6.1x $10^{14}$ |

Table 1. Compositions, mean atomic numbers and critical amorphisation doses of samples.

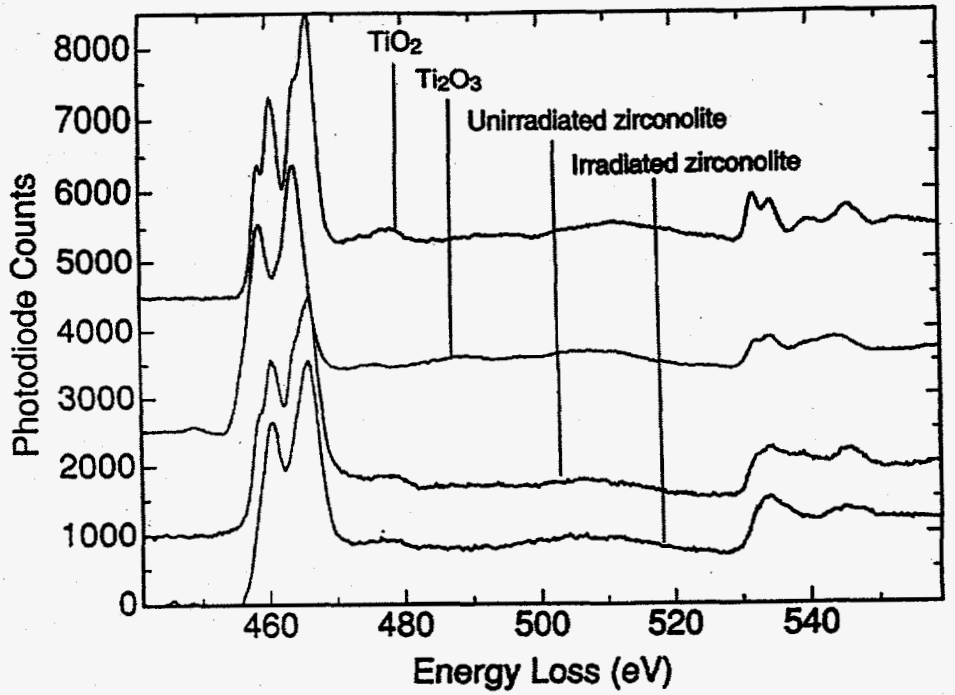


Figure 2. EELS spectra of $TiO_2$, $Ti_2O_3$, unirradiated and irradiated undoped zirconolite.