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EXAFS STUDIES OF METAMICT MATERIALS

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An important approach in the evaluation of crystalline wasteforms for nuclear waste storage is to study the long term stabilities of closely related radioactive mineral species which have become metamict (radiation damaged) and have been exposed to weathering processes for geologic periods of time. The metamictization and alteration effects can then be used for comparison with the results of short term laboratory leaching and irradiation experiments which have been designed to simulate long term effects. Phosphates, the Ti-Nb-Ta complex oxide minerals and various selected silicates are natural analogues for phases in proposed radioactive wasteforms. Because of the geochemical similarities with wasteforms, a study of the metamict state and annealing in complex mineral phosphates, silicates and oxides will yield data that is important in evaluating the long term stability of radioactive wasteforms.

The investigation reported here is an application of EXAFS and XANES spectroscopy to the study of the structure of the metamict state. The nearest neighbor environment of Ti and Ca in metamict AB_2O_6-type complex oxides have been examined using SSRL Beam Line VII-3 in order to evaluate the effect of alpha-recoil damage on these structures. Comparison of the EXAFS/XANES data for metamict samples with data for annealed and crystalline samples suggests minor changes in the first coordination sphere, Ca-O or Ti-O, (a slight decrease in coordination number and bond lengths, and increased distortion of the coordination polyhedron), but major disruption of the second coordination sphere, for the material in the metamict state. These data suggest a mechanism for the transition from the crystalline to the metamict state in which tilting of cation coordination polyhedra is a possible effect of damage caused by alpha-recoil events.

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1. Introduction

Radiation damage effects and the kinetics of annealing in crystalline materials are important in the evaluation of the long-term stability of crystalline radioactive waste forms. The selection of a radioactive waste form which will maintain its chemical and physical integrity for periods of 10^4-10^6 years requires a thorough understanding of the structural and bonding controls on radiation damage, as well as the thermal conditions under which the alpha, alpha-recoil and fission fragment damage will be annealed. One approach in evaluating these effects is to study the transition from the crystalline to the metamict state in naturally occurring minerals which contain uranium, thorium and their daughter products. Metamict minerals are a special class of "amorphous" materials which were initially crystalline, but due to damage caused by alpha particles and their recoil nuclei have become "X-ray diffraction amorphous." Recent simulations of the metamictization process have included a variety of techniques but these simulation experiments generally have not been validated by comparative studies of the properties of irradiated materials with those observed in natural metamict minerals of great age. This paper summarizes the results of EXAFS and XANES spectroscopy on the evaluation of the coordination geometries of Ti [1] and Ca [2] in selected natural metamict minerals.

2. Samples and Experimental Technique

The metamict Ti-Nb-Ta oxides of the type formula $A_xB_yO_z$ (A = lanthanides, Fe^{2+}, Mn, Na, Ca, Th, U, Pb; B = Ti, Nb, Ta, Fe^{3+}) include three structure types investigated here whose ideal formulas are represented by euxenite, $YNbTiO_6$, aeschynite, $CeNbTiO_6$ and zirconolite, $CaZrTi_2O_7$. The nomenclature and crystal chemistry for these minerals are summarized by EWING and CHAKOUMAKOS [3]. In the high temperature euxenite structure (Pcan), B-site cations have six-fold coordination; and A-site cations, eight-fold coordination. The B-site octahedra are slightly distorted and connected along two edges into zig-zag chains. These chains are arranged into two-dimensional layers that are connected by single layers of A-site cations. Blomstrandine is a low temperature priorite - aeschynite (Pbnm) structure type, where A and B site cations have eight and six fold coordination respectively, but B site octahedra are joined in pairs along edges, and each pair is connected to another pair of B-site octahedra at the apices and thus form zig-zag three-dimensional chains. Sample R25 (euxenite) was annealed to the high-temperature structure type (1100°C for 60 h), sample R13 (blomstrandine) to the low-temperature structure type (510°C for 52 h). For comparison, synthetic standards of the euxenite structure type ($YNbTiO_6$) and aeschynite structure type

($LaNbTiO_6$) were prepared. Zirconolite (C2/c, Z = 8) is a fluorite related superstructure [4] similar to pyrochlore. The structure has sheets of $Ti(Zr)O_6$ octahedra sharing corners in three- and six-membered ring arrangements. These sheets are interleaved by planes containing Ca and Zr(Ti) atoms ordered into alternating rows with Ca coordinated by eight oxygens and Zr(Ti) coordinated by seven oxygens. A Ti atom close to the center of a six-membered ring arrangement occupies one of a pair of sites which is five-fold coordinated by O. For comparison both metamict and annealed (1100°C for 2 hours) zirconolite were examined as well as several Ca standard reference compounds.

The EXAFS/XANES experiments were performed at the Stanford Synchrotron Radiation Laboratory (SSRL). At SSRL the side station of Beam Line VII (a Wiggler line) was used, with the synchrotron beam at a current of approximately 60 mA and an energy of 3 GeV. A Si(220) double crystal monochromator was used for the Ti K-edges and a Si(111) for the Ca K-edges. The angle between the crystal faces was adjusted to detune the diffracted beam by 50% in order to reduce the harmonic content of the beam in the sample chamber. The monochromator was moved in 0.25 eV steps in the vicinity of the K-edge. The data was gathered at room temperature using a fluorescent X-ray detector [5]. Nitrogen was used in the I_0 and I chambers, with He in the sample holder area to enhance transmission of the X-rays and minimize background scattering.

3. Ti K-Edge Results

Evidence of significant geometrical rearrangement due to radiation damage at the Ti site is illustrated in Figs. 1 and 2 which show the Fourier transforms of the $\chi(K)$ of the unannealed, annealed and synthetic standards for R13 and R25. The first major peaks in the transform (indicated by arrows in the figure) are due to first neighbor oxygen atoms around Ti. The peaks at low R values are an artifact of the data analysis and are not due to coordinating atoms. Although the first neighbor oxygen peaks show interesting differences, the most striking feature in the Fourier transforms is the second neighbor peak. For both the R13 and R25 sets of Fourier transforms there is a substantial enhancement of the second neighbors for the standard and annealed samples as compared to the unannealed samples. This suggests that the metamictization process has the effect of disordering the second neighbors around the Ti (i.e., the metal-metal coordinated sphere).

To investigate the more subtle differences in the first neighbor oxygen peaks, inverse Fourier transforms where performed on these peaks. The resulting $\chi(K)$ functions were then analyzed using iterative nonlinear least-squares curve fitting techniques. At this point in the analysis the least square fitted values are expected to have fairly large errors. This analysis only suggests trends, rather than allowing the assignment of precise values of coordination number, bond length and disorder.

The results suggest that in the metamict state (i.e., prior to annealing) the first neighbors are reduced by 10-20%, with most of the reduction being due to loss of the longer (i.e., > 2.0 Å) bonded oxygens. Also a slight contraction in the average bond length was seen in the metamict samples. The picture that emerges from this annealing study is that the effect of radiation damage at the Ti-site is to disrupt the nearby oxygen atoms increasing the asymmetry, with even greater disruption in the second neighbor metal atoms.

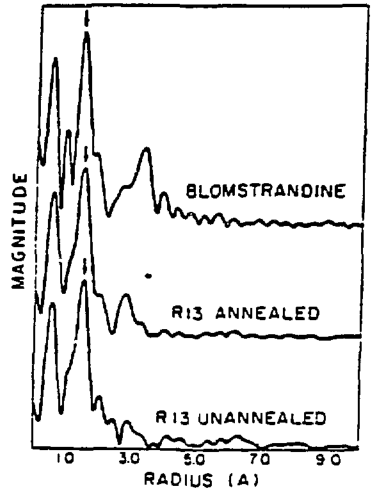

Figure 1. Fourier transforms of Ti K-edge EXAFS of synthetic blomstrandine, R13 annealed, R13 unannealed

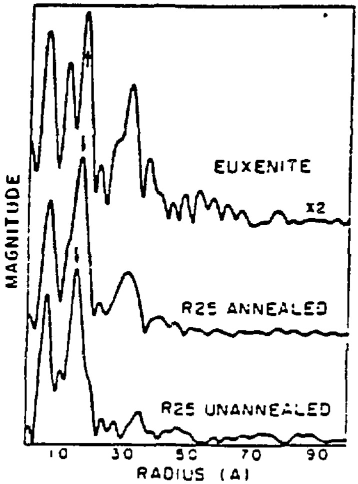

Figure 2. Fourier transforms of the Ti K-edge EXAFS of synthetic euxenite R25 annealed, and R25 unannealed

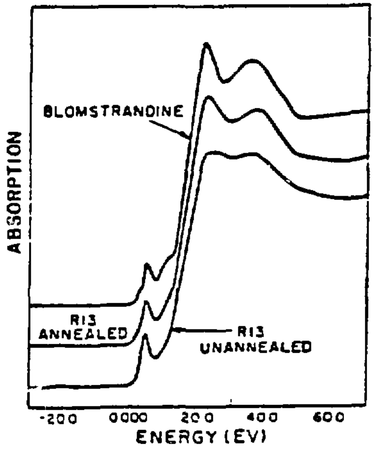

Figure 3. Ti K-edge XANES of synthetic blomstrandine, R13 annealed, and R13 unannealed

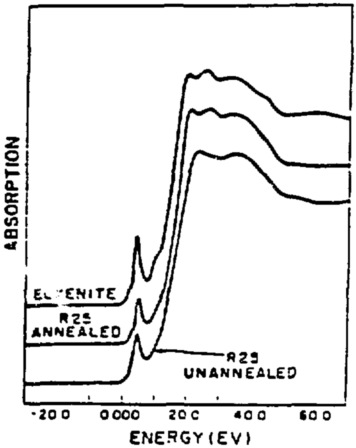

Figure 4. Ti K-edge XANES of synthetic euxenite, R25 annealed, and R25 unannealed

A comparison of the XANES of the unannealed, annealed and synthetic standards is shown in Figs. 3 and 4. Interestingly, the unannealed samples of both R13 and R25 have remarkably similar XANES. After annealing however, the XANES of R13 and R25 show significant differences. As expected, they no longer resemble each other but instead are similar to the XANES of their crystalline counterparts. The height of the pre-edge feature is indicative of the degree of asymmetry around Ti [6]. In the unannealed R13 and R25 samples the pre-edge height is ∿ 15% and ∿ 9% higher, respectively, than the corresponding annealed samples. This provides further support that one effect of radiation damage is to increase the degree of asymmetry in the Ti-O polyhedra. In addition to site symmetry, the oxidation state of Ti can also be inferred. Examination of the edge shifts of the annealed and unannealed metamict samples indicates that, within the accuracy of the technique, all of the Ti is in a 4^+ oxidation state.

4. Ca K-Edge Results

The Ti atoms in the standard structure types are located at the center of an octahedron of oxygen atoms with the edges or apexes of the octahedra connected to form a network whose voids are filled with other atoms such as Ca. The Fourier transforms of the Ca K-edge EXAFS of the natural (unannealed) and annealed samples are shown in Figs. 5 and 6. The data for euxenite sample were not of high quality. From the transforms we see that the natural samples have lower second coordination shell magnitudes than do their annealed counterparts. The observed change in the second coordination shell around the Ca is consistent with the observations of the Ti site previously discussed. That is, the second coordination sphere has undergone substantial rearrangement as a result of the metamictization process. Our interpretation of this data is that the change in the higher coordinating atoms is due to increased disorder as these crystalline phases proceed to a more glass-like random network.

Inverse Fourier transforms were performed on the first oxygen coordinating shells around the Ca for the zirconolite sample. The resultant spectra for the annealed and natural samples were then compared using the ln of the ratio technique. This analysis showed that the average 1st shell oxygen coordination number was reduced in the metamict sample so that N(Nat)/N (Ann) = .62 and the disorder σ^2(Nat) - σ^2(Ann) = - .001 Å^2.

Using this result as a guide we proceeded to a nonlinear least square fit of the inverse 1st shell spectra. The initial trial values for the fit to the annealed data were obtained from the X-ray diffraction studies on zirconolite by GATEHOUSE [4]. The eight Ca-O distances were combined into three sub-shells (N_1 = 4, N_2 = 1, N_3 = 3) for the first coordinating oxygen shell around the Ca. The EXAFS phase and scattering amplitude were obtained from a Ca-O standard. The R values were held fixed, and N and σ allowed to vary so that the ratio of N_1:N_2:N_3 was 4:1:3. The values from the fit to the annealed spectra were then adjusted so that the sub-shell N values were 75% (using as a guide the 62% reduction indicated by the ln of the ratio technique) and the sub-shell R values were 98% (using the peak positions of the Fourier transforms) of the annealed fitted values. The σ value was the only free variable in the fitting of the metamict spectra which resulted in a good fit of the data. Thus we see the fit results of the Ca sites are in qualitative agreement with the Ti sites. Upon being damaged by alpha-recoil nuclei events the overall 1st shell coordination is reduced with a slight decrease in bond length of the coordinating oxygen atoms.

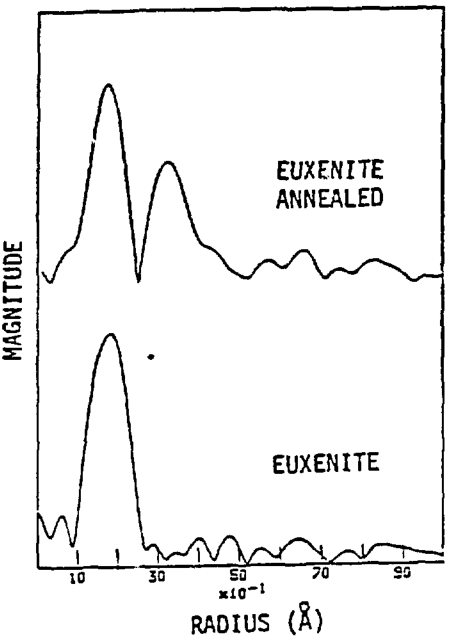

Figure 5. Fourier transforms of Ca K-edge EXAFS of natural and annealed euxenite

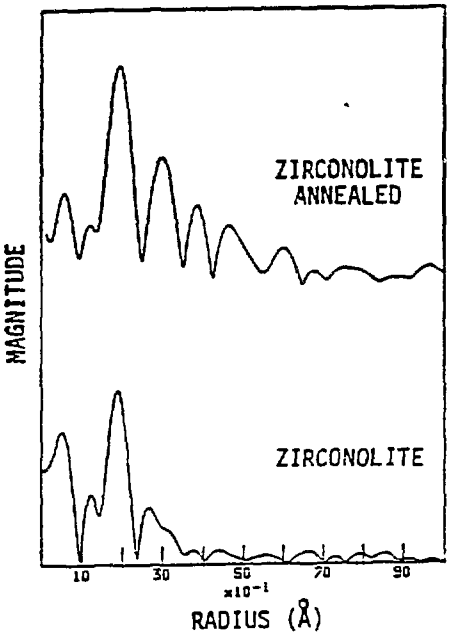

Figure 6. Fourier transforms of Ca K-edge EXAFS of natural and annealed zirconolite

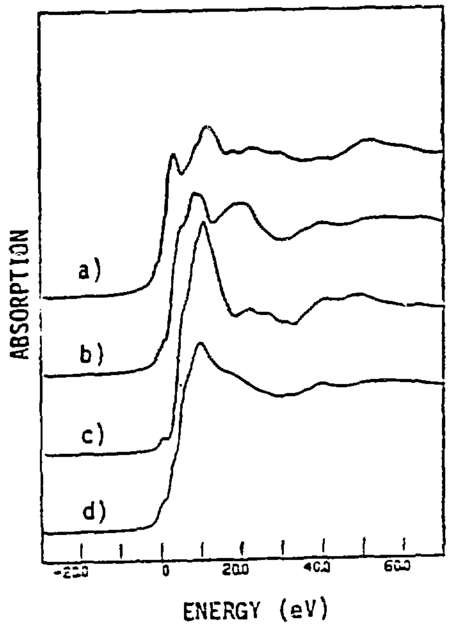

Figure 7. Ca K-edge XANES of standard reference materials; a) CaO, b) $CaCO_3$, c) gypsum, d) Ca acetate [6]

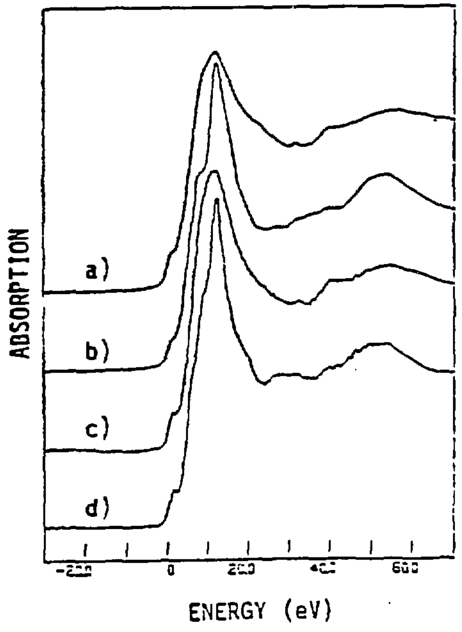

Figure 8. Ca K-edge XANES of a) zirconolite natural, b) zirconolite annealed, c) euxenite natural and d) euxenite annealed

The Ca K-edge XANES of several standard materials is shown in Fig. 7 and the XANES of the natural and annealed euxenite and zirconolite samples in Fig. 8. The natural metamict specimens show a similar signature which is comparatively broadened with a small shoulder on the low energy side of the first major peak. The annealed samples all show narrower main peaks, the same shoulder on the low energy side of the major peak and the addition of a step on the steep increase of the major peak. The general sharpening and finer resolution of the spectral features was also seen in the Ti edge XANES. The leading edges of the first major peaks of both natural and annealed samples were within $\sim$ 1 eV of each other and all were displaced $\sim$ 4 eV higher in energy as compared to the Ca-O standard.

5. Conclusion

The nearest neighbor environment of Ti and Ca in selected metamict Nb-Ta-Ti complex oxides have been examined in order to evaluate the effect of alpha-recoil damage on these structures. Comparison of the EXAFS/XANES data for metamict samples with data for annealed and crystalline samples suggests minor changes in the first coordination sphere, Ti-O or Ca-O, but major disruption of the second coordination sphere, for the material in the metamict state. These data suggest a mechanism for the transition from the crystalline to the metamict state in which tilting of cation coordination polyhedra is a possible effect of damage caused by alpha-recoil events.

Acknowledgements

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6. Ca standards courtesy of G. P. Huffman and F. E. Huggins, U. S. Steel Corporation, Monroeville, PA.