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Nanoscale Diffusion of Lead in 300Ma Old UTi_2O_6 Mineral

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Brannerite, ideally $(U,Th)_{1-x}Ti_{2+x}O_6$, is a monoclinic accessory phase that is completely metamict (amorphous) as a result of the α-decay damage from the constituent U and Th [1]. Its structure can be re-crystallized on heating. Many cation substitutions have been identified for both uranium (Pb, Ca, Th, Y and Ce) and titanium (Si, Al, Fe) in natural brannerites. Brannerite is also formed in the titanate-based nuclear waste-form ceramics processed under reducing conditions.

Particles of natural brannerite were examined using a FEI Helios 660 NanoLab™ FIB and standard lift-out specimens were prepared. The porous nature of the natural specimens required additional carbon-deposition steps to produce quality specimens. Lift-out specimens of the natural mineral and crushed specimens of the synthetics were characterized in a JEOL GrandARM™ 300F probe corrected STEM operated at 300 kV located in the Radiochemical Microscopy Suite in the Radiochemical Processing Laboratory at PNNL. The microscope was equipped with High Angle Annular Dark Field (HAADF) detectors, a Gatan Image Filter, and dual Bruker EDS detectors. Synthetic and natural specimens of brannerite were examined by x-ray absorption spectroscopy at the Synchrotron Radiation Center (SRC) in Stoughton, WI at the HERMON beamline. The O-K and Ti-$L_{2,3}$ edges were probed in detail with a resolution of ~0.1 eV [2].

We observed the formation of bubbles throughout the matrix (see Figure 1A). These may have been the result of the accumulation of helium in the structure from α-decay. Some regions of the sample had high levels of silicon suggesting chemical alteration of the material had occurred. Excess uranium appeared to have precipitated heterogeneously throughout the material. Diffraction analysis reveal that these particles were crystalline UO_2 (see Figure 1A inset); whereas, all other areas were amorphous. Elemental analysis was performed with a combination of EDS and EELS to reveal nanoscale variations in composition. The lead-rich regions were easily identifiable in the HAADF and BF images of the material but were revealed more clearly with EDS mapping. Pockets of rare earths were also found with EELS mapping. The structure was compared to a synthetic Ce-brannerite that was well crystallized (see Figure 2A). XANES of the oxygen K-edge was compared to a synthetic brannerite and indicated the large changes in the coordination environment for O. However, the Ti-$L_{2,3}$ edge showed very little difference between the natural and synthetic forms (see Figure 2B). This suggests that the local Ti environment has not changed during the radiation damage process. As oxygen was present in several different phases, the complex O-K edge should not be surprising [3]. As previously described by Lumpkin et al.[1], lead was also associated with silicon in the altered mineral [3].

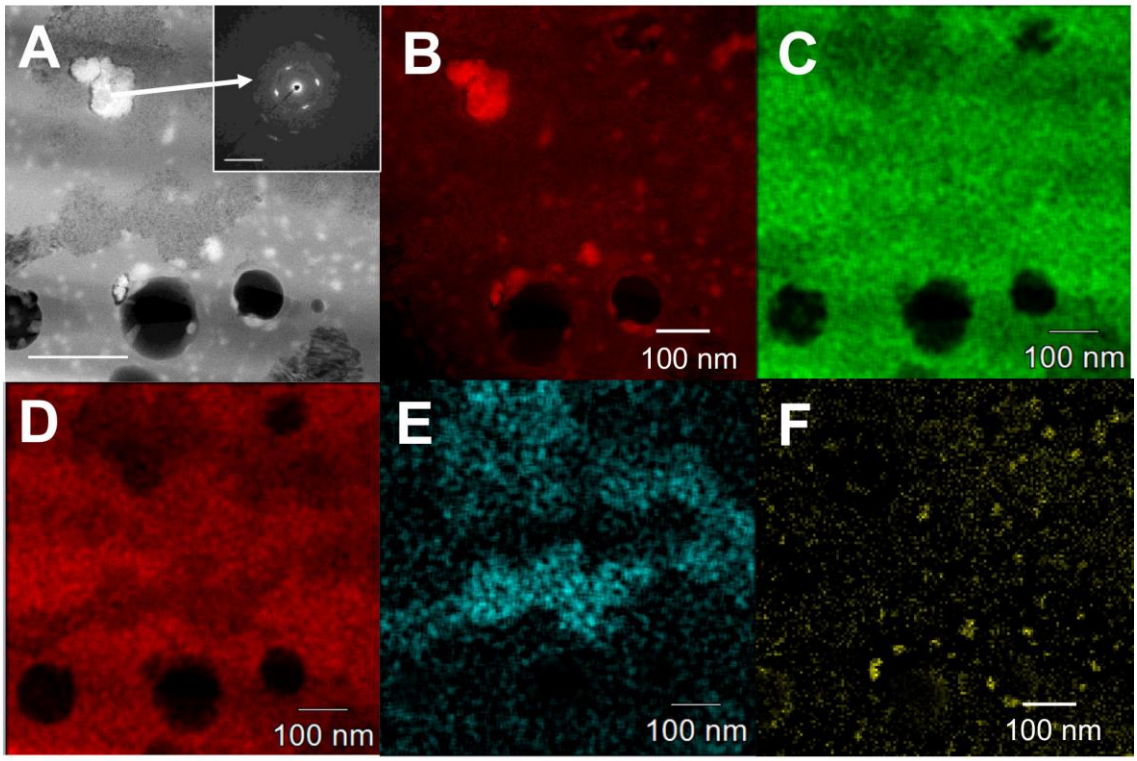

Figure 1. Figure 1. (A) HAADF image of brannerite mineral and insert diffraction pattern from the bright region (UO2), containing regions (B) uranium (U-O4,5 edge), (C) oxygen (K line), (D) titanium (K line), (E) lead (L-line), and (F) lanthanum (M4,5 edge), showing the migration of lead from the major phase as well as the formation of UO2 crystals within the matrix. Voids are visible in the image from helium bubbles from α-decay.

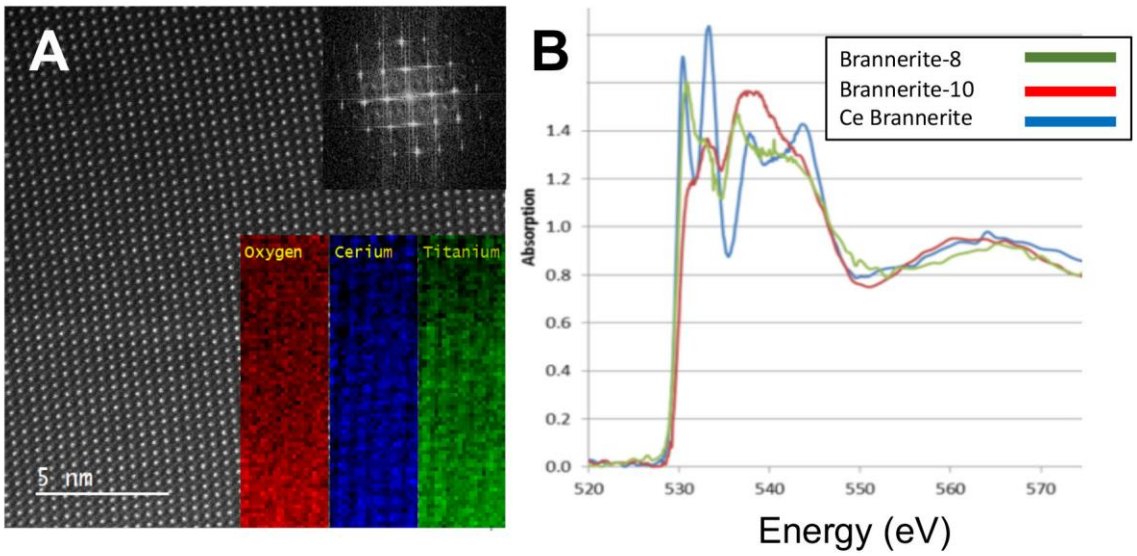

Figure 2. Figure 2. (A) HAADF atomic resolution image of synthetic brannerite and EELS maps (insert) and (B) bulk XANES analysis of the O-K edge from the natural and synthetic brannerites.

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