

Crystal Chemistry, Alpha Decay Damage, and Geochemical Alteration of Brannerite and Davidite

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Abstract: To investigate the long-term stability of the uranium minerals brannerite and davidite, we have undertaken an electron microscopy study of samples from a range of geological environments worldwide. Our results indicate that both minerals are transformed to an amorphous phase after a dose of approximately $10^{16} \alpha \text{ mg}^{-1}$, similar to other rare element oxide minerals. Both minerals are susceptible to alteration via interaction with hydrothermal fluids, although by different mechanisms. The U-Th-Pb chemical ages of brannerite are generally consistent with the known ages and geological histories of the host rocks. These ages are affected by U loss from altered areas and Pb loss from unaltered brannerite.

Introduction: Brannerite, ideally UTi_2O_6 , is a common accessory phase in special purpose, pyrochlore-rich titanate ceramics designed for the encapsulation of actinide-rich nuclear wastes. In particular, the pyrochlore-rich waste forms are candidates for the long-term storage of surplus Pu in the United States, Russia, and the United Kingdom. Designs in the United States, circa 2000, called for ceramic pucks containing about 35-40 wt% TiO_2 , 20-25 wt% UO_2 , 10 wt% PuO_2 , 10 wt% HfO_2 , 7-10 wt% Gd_2O_3 , and 8-12 wt% CaO [1]. Davidite, ideally $\text{AM}_{21}\text{O}_{38}$, is a complex Fe-Ti oxide mineral of the crichtonite group. Another member of this group, lovingite, occurs as a minor phase in Synroc-C and related ceramics for the immobilization of high-level nuclear wastes from commercial power generation. These minerals are of further interest as they are important carriers of U and rare earth elements (REE) in Australian granitic rocks, e.g., in parts of the Olary block of South Australia.

Experimental: SEM-EDX work was carried out on polished sections using a JEOL JSM-6400 SEM and Noran Voyager Si(Li) microanalysis system, including an ultra-thin window detector with a nominal resolution of 134 eV on the Mn $K\alpha$ x-ray peak. EDX spectra were acquired for 500 seconds and processed using Noran software. TEM was performed on crushed fragments dispersed on holey carbon grids using a JEOL 2000FXII TEM equipped with a Link ISIS Si(Li) microanalysis system. The EDX detector is of the ultra-thin window type and has a nominal resolution of 129 eV on the Mn $K\alpha$ x-ray peak. Spectra were acquired for 600-900 seconds and processed with the Link ISIS software package TEMQuant.

Brannerite: The compositions based on SEM-EDX analyses indicate that these natural brannerites contain 36-42 wt% TiO_2 , 30-57 wt% UO_2 , 0-15 wt% ThO_2 , 0-7 wt% CaO , 0-7 wt% PbO , 0-2 wt% Nb_2O_5 , 0-3 wt% SiO_2 , 0-2 wt% Al_2O_3 , 0-3 wt% Fe_2O_3 , and 0-8 wt% REE_2O_3 . Both MnO and NiO were detected in various samples but it is unusual for these metal oxides to reach levels of 0.5-1.0 wt%. The main substitutions are Fe+Al for Ti on the B-site and Th for U on the A-site. Altered regions of brannerite contain significant amounts of Si and other elements incorporated from an aqueous fluid phase, and up to 40-90% of the original amount of U has been lost as a result of alteration. SEM-EDX results also provide evidence for TiO_2 phases, galena, and a thorite-like phase as alteration products. Electron diffraction patterns of all samples typically consist of two broad, diffuse rings that have equivalent d-spacings of 0.31 nm and 0.19 nm, indicating that brannerite is rendered completely amorphous by alpha decay damage. Using the available age data, the samples have accumulated alpha decay doses in the range of $0.7\text{-}200 \times 10^{16} \alpha \text{ mg}^{-1}$. Based on one

literature report [2], the critical dose for amorphization is approximately $10^{16} \alpha \text{ mg}^{-1}$. U-Th-Pb chemical ages determined by microanalysis are generally consistent with the known ages and geological histories of the brannerite host rocks. Calculated ages are mainly affected by U loss from altered areas and Pb loss from unaltered areas. Radiogenic Pb tends to be retained by the Ti-Si-O glass-like network of altered brannerite and in secondary galena particles where S is a component of the local system.

Davidite: SEM-EDX analyses demonstrate that the chemical composition varies considerably from sample to sample, but individual samples are relatively uniform in composition with only limited evidence for zoning. For the samples investigated in this study, the U content ranges from approximately 0.2 to 9.5 wt% UO_2 (0.02 to 0.65 atoms per formula unit). The Th content is much lower, ranging from < 0.1 to 1.3 wt% ThO_2 (< 0.01 to 0.09 atoms per formula unit). Maximum amounts of other components include 3.7 wt% V_2O_5 , 4.1 wt% Cr_2O_3 , 2.5 wt% Y_2O_3 , 5.6 wt% La_2O_3 , 6.0 wt% Ce_2O_3 , 4.0 wt% MnO , 2.4 wt% ZnO , 2.7 wt% SrO , and 4.9 wt% PbO . The amounts of Ti and Fe atoms are relatively constant in the formula unit, the main variations being the contents of other transition metals in the M block and large cations such as light REE, Sr, Pb, Th, and U on the A-site. Based on the age and U content, the samples have accumulated alpha decay doses in the range of $0.2\text{--}44 \times 10^{16} \alpha \text{ mg}^{-1}$. TEM work shows that many samples are also amorphous above a critical dose of approximately $10^{16} \alpha \text{ mg}^{-1}$. Davidite is commonly altered to a secondary phase assemblage consisting of ilmenite, Fe-oxides, and other phases, releasing U and REEs to the local system.

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References

- [1] D.M. Strachan, R.D. Scheele, E.C. Buck, J.P. Icenhower, A.E. Kozelisky, R.L. Sell, R.J. Elovich, and W.C. Buchmiller, "Radiation damage effects in candidate titanates for Pu disposition: Pyrochlore," *J. Nucl. Mater.*, vol. 345, pp. 109-135, 2005.
- [2] S. Graeser and R. Guggenheim, "Brannerite from Lengenbach, Binntal (Switzerland)," *Schweiz. Mineral. Petrogr. Mitt.*, vol. 70, pp. 325-331, 1990.

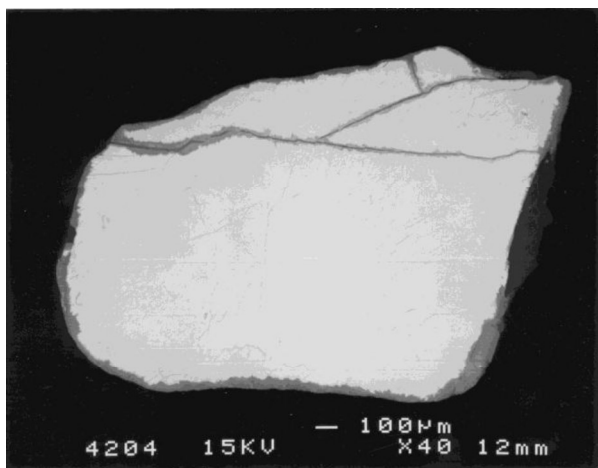


Fig.1. Fully amorphous brannerite from Idaho showing partial alteration around the rim of the grain and along cracks.

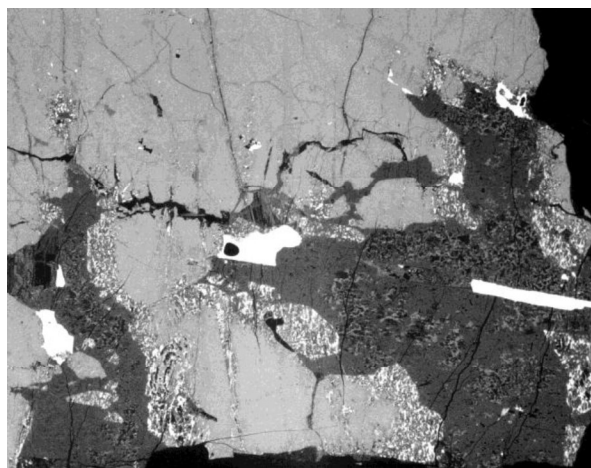


Fig. 2. Backscattered electron images of heavily radiation damaged and partially altered davidite from Iveland, Norway. Width of image is 1.3 mm.