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Alteration of coffinite under reducing and oxidizing conditions

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Coffinite, $USiO_4$, is a one of the two naturally occurring actinide silicates (second is thorite, $ThSiO_4$) studied to elucidate the alteration of spent nuclear fuel (SNF) under reducing conditions in a Si-rich environment. In order to understand the stability of coffinite under different redox condition in natural systems, we have investigated coffinite the Grants Uranium Belt, New Mexico, USA (reducing and oxidizing conditions) utilizing a variety of electron microbeam techniques.

Fine-grained coffinite ($\leq$10 μm) from Woodrow Mine coexists with carbonate-fluorapatite (CFAp) and (Ca,Sr)-(meta)autunite (M-Aut). It precipitated under reducing conditions replacing CFAp, pyrite and aluminosilicates. Electron-microprobe analyses (EMPA) of coffinite indicate limited incorporation of P_2O_5 and CaO, below 2.7 and 3.0 wt.%, respectively, into the coffinite structure during replacement of CFAp. The chemical formula of coffinite is $(U_{0.95\pm0.09}Ca_{0.15\pm0.02})_{\Sigma1.10\pm0.1}(Si_{0.84\pm0.08}P_{0.06\pm0.02})_{\Sigma0.90\pm0.08}$. Analysis by high-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM) revealed that coffinite initially formed as crystals as large as 100 nm at the edges of altered CFAp. Subsequently, infiltration of (Na,Ba,Sr)-rich oxidizing fluids into fractures resulted in precipitation of Sr-rich M-Aut (up to 4 wt.% of SrO) at the expense of coffinite and CFAp. High-resolution TEM reveals that Na-rich fluids caused a distortion of the ideal coffinite structure and stabilized amorphous domains that formed due to alpha-decay event radiation damage. Subsequently, the Na-enriched amorphous areas of coffinite were preferentially altered, and secondary porosity formed at the scale of $\sim$1 μm. Porosity also was formed during alteration of CFAp to M-Aut, which facilitated the migration of oxidizing fluids over distances of $\sim$150 μm into CFAp, as evidenced by precipitation of M-Aut.

These results show that micro-scale dissolution of apatite can create conditions conducive to the precipitation of U(IV)- and U(VI)-minerals, leading to the reduced mobility of U-species under both reducing and oxidizing conditions. It is concluded that coffinite typically precipitates as micron- to nano-sized crystals within an amorphous matrix and is highly stable under reducing conditions. The infiltration of Na-rich fluids into the amorphous domains in coffinite prevented recrystallization by thermal annealing. It can be considered that the amorphous domains were stabilized by the presence of Na. In contrast, coffinite is altered extensively under oxidizing conditions and releases U into the ambient system, however, the released U is immediately sequestered by the precipitation of secondary uranyl minerals.