Degradation of Cu-bearing uranyl As-P micromineral phases from Krunkelbach uranium deposit, Southern Germany

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The abandoned Krunkelbach uranium (U) mine, Southern Germany, with 2-3 km surrounding area represents a unique natural analogue site with accumulation of U minerals suitable for investigations of potential mobilization-immobilization processes expected in a real spent nuclear fuel repository. A specific feature of the site is the occurrence of more than forty secondary U minerals, from mixed redox U oxy-hydroxides to alkaline metal uranyl silicates, thus representing a wide scale of U ore weathering events. In this work the combination of synchrotron and laboratory techniques is used to unveil U speciation and micro heterogeneities in U phases accumulated on granitic rock outcrop from U deposit area. Available data on the age of the secondary U mineralization indicates that oxidizing processes at the site started some 340,000 years ago and continues up to date. Several phases close to $Cu(UO_2)_2(PO_4)_{2-x}(AsO_4)_x \cdot 8H_2O$ are identified on 1×2 mm^2 area with presumably older, more evenly distributed $Cu(UO_2)_2(SiO_3OH)_2 \cdot 6H_2O$ and (Fe, Ba, Pb)$(UO_2)_2(WO_4)$ $(OH)_4 \cdot 12H_2O$, mineralization. Based on a multi-technique investigation 10-200 µm $Cu(UO_2)_2(PO_4)_{2-x}(AsO_4)_x \cdot 8H_2O$ particles with widely varying As-P content are analyzed. The evidences of a degradation occurred on some zones on the selected crystals are found associated with higher As and decreased P content. This observation can be apparently attributed to different degradation properties of the mixed As-P phases depending on As-P ratio and originate from different solubility properties of $Cu(UO_2)_2(PO_4)_2 \cdot 8H_2O$ and $Cu(UO_2)_2(AsO_4)_2 \cdot 8H_2O$ species. The conditions for preferential formation of As rich $Cu(UO_2)_2(XO_4)_2 \cdot 8H_2O$ [X=As, P] phases and its possible role on U transport in environment under oxidizing conditions are discussed.