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Fate of the epsilon phase in the Oklo natural reactors

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In spent nuclear fuel (SNF), the micron- to submicron-sized epsilon phase (Mo-Ru-Pd-Tc-Rh) is an important host of ^{99}Tc which has a long half life (2.13×10^5 years) and can be an important contributor to dose in safety assessments of nuclear waste repositories. In addition, Tc is predominantly present as TcO_4^- under oxidizing conditions at wide range of pH, weakly adsorbed onto mineral surfaces, and unlikely to be incorporated into alteration uranyl minerals. In the Oklo natural reactor (2.0 Ga), essentially all of the ^{99}Tc has decayed to ^{99}Ru. Thus, this study focuses on Ru and the other metals of the epsilon phase in order to investigate the occurrence and the fate of the epsilon phase during the corrosion of this natural SNF. Samples from reactor zone (RZ)-10 (836, 819, 687); from RZ-13 (864, 910); were investigated using TEM (transmission electron microscopy).

Within the UO_2 matrix, a Bi-Pd particle (40-60 nm), froodite, $PdBi_2$, was observed with trace amounts of As, Fe, and Te surrounded by an amorphous Pb-rich area. $(Pd,Rh)_2As$, palladodymite or rhodarsenide, was observed (400-500 nm in size). Ruthenarsinite, (Ru,Ni)As, was identified in most samples: with a representative composition of As, 59.9: Co, 2.5: Ni, 5.2; Ru, 18.6; Rh, 8.4; Pd, 3.1; Sb, 2.4 in atomic percent. The particles diameters are a few hundred nanometers and, in most cases, surrounded by a Pb-rich phase (400-500 nm). Typically, the ruthenarsenite does not occur as single particle but an aggregate of ~200 nm-sized particles. Some Ru-particles revealed a complex phase separation within the grain such as a Ru-particle (600-700 nm) with Pb at the core of the particle and enrichment of Ni, Co, and As at the rim. Some ruthenarsenite crystals were embedded in chlorite immediately adjacent to uraninite. A few particles were still coated by Pb. These results suggest a history for the epsilon phases: (i) The original epsilon phase was transformed to, in most cases, ruthenarsenite. (ii) All Mo and most of the Tc were released from the epsilon phase. Some portion of the other metals was also leached and provided a space for a precipitation of PbS between the ruthenarsenite and uraninite. (iii) Once the uraninite matrix dissolved, the epsilon particles were released and sometimes captured within adjacent alteration minerals.