15th V.M. Goldschmidt Conference in Moscow, Idaho, May 20-25, 2005

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The epsilon phase in the UO_2 of the Oklo natural reactors

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In spent nuclear fuel (SNF), the metal epsilon phase consists of an alloy of Mo-Ru-Pd-Tc-Rh, occurring at a micron to sub-micron scale. ^{99}Tc 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. Under oxidizing conditions, TcO_4^- is the predominant species of Tc. In this form, Tc is highly soluble and weakly adsorbed onto mineral surfaces. Because the Oklo reactors are 2.0 billion years old, a majority of the ^{99}Tc formed by natural fission reactions has decayed to ^{99}Ru. Thus, this study is focused on Ru and the other constituents of the epsilon phase in order to investigate the occurrence and the fate of epsilon phase elements during the corrosion of this natural SNF.

Samples from reactor zone (RZ)-10 (836, 819, 687); from RZ-13 (864, 910); from Okélobondo (943) were studied. High resolution transmission electron microscopy (HRTEM) and high-angle annular dark-field scanning TEM (HAADF-STEM) with energy dispersive X-ray analysis (EDX) were completed on thin foil specimens of uraninite from each reactor zone. Among these samples, no Ru-bearing phase is observed in 910 and 943.

A Bi-Pd particle (40-60 nm), froodite, $PdBi_2$, occurs with trace amounts of As, Fe, and Te surrounded by an amorphous Pb-rich area (#864). A Ru-As particle (~300nm) occurs surrounded by Pb-rich inclusion (400-500nm) in uraninite (#819). Based on EDX analysis the composition is: As, 59.9: Co, 2.5: Ni, 5.2; Ru, 18.6; Th, 8.4; Pd, 3.1; Sb, 2.4 in atomic%. The Ru-As phase is not a single particle, but an aggregate of 100-200 nm-sized ruthenarsenite, (Ru,Ni)As, particles. Another Ru-particle (600-700 nm) shows that Pb occurs at the core of the particle, and the rim portion consists of Ni, Co, and As without Ru (#819). Ru-particles, ruthenarsenite, occur with Ni between the core and the rim. A Mo-particle (<50 nm) is embedded in a polycrystalline galena (#836). A Ru-particle occurs in a Pb-inclusion in the presence of two phases within the particle: Ru; As-rich part and Pd; Rh-rich area. The Pd-Rh-rich area occupies the center of the particle, and Ru-rich region occurs at the edge of the particle. The EDX spectrum of the Pd-Rh-rich part revealed some As. Semi-quantitative analysis gives: 16.0 As, 5.8 Ru, 26.7 Rh, 39.2 Pd, 2.8 Sn, and 9.4 Sb in atomic%. Because there ae a limited number of possibilities for a natural mineral that contains both Pd and Rh, the phase is either palladodymite or rhodarsenide, both of which are $(Pd, Rh)_2As$.

All of the Ru-phases are associated with polycrystalline galena. There is a wide variation in the composition of the Ru-phase. The Ru-particles are, in most cases, ruthenarsenite, and do not contain detectable amounts of Mo, although the Mo-concentration for the epsilon phase in SNF is reported to be as high as 40 atomic%. Mo is only observed as a separate nano-scale phase in a nanocrystalline aggregate of galena.