

Micro-x-ray Fluorescence Analysis of Fission Product Retention and Migration in the Oklo (Gabon) Natural Fission Reactors

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Introduction

The successful disposition of used nuclear fuel is one of the most significant challenges to the future of nuclear power generation. In the proposed nuclear waste repository at Yucca Mountain, more than 95% of the radioactivity will originate from spent nuclear fuel. Spent nuclear fuel is essentially UO_2 with approximately 4-5 at. % actinide and fission product elements, many of which have long half lives (e.g., $^{239}\text{Pu} = 24,500$ yr, $^{237}\text{Np} = 2$ million yr, and $^{129}\text{I} = 16$ million yr). One of the most difficult aspects of understanding the behavior of spent nuclear fuel in a geologic repository is the extrapolation of short-term laboratory data (hours to years) to the long time periods (10^3 - 10^5 years) required by U.S. Environmental Protection Agency regulations (i.e., *Code of Federal Regulations*, Title 10, Part 60 [10 CFR 60]). One means of confirming long-term extrapolations is through the study of natural analogues. One such site is in Gabon, Africa, where the Oklo natural fission reactors operated 2 billion years ago. The Oklo natural fission reactors represent the only known location in the world where sustained *natural* fission reactions took place [1]. During any fission event, hundreds of fission products are produced, but they are generally at very low concentrations. The highest concentrations of fission products are at atomic masses of 90 and 140 (i.e., zirconium and cerium). Combined, these fission products make up ~4 wt% of the UO_2 . By using micro-x-ray fluorescence (XRF) to determine the qualitative and quantitative fission product distribution in UO_2 point analysis and mapping, we will be able to better understand the retention and migration of fissionogenic elements under reducing and oxidizing conditions at the microscale (i.e., within an individual UO_2 grain) and macroscale (i.e., the spatial behavior in and around the reactor zone).

Methods and Materials

The main benefits of micro-XRF at the APS are the combination of the low detection limits of the XRF, the high spatial resolution provided by a focused beam, and, most importantly for this work, the high energies (>50 keV) available on the APS beamline. The high flux of the beam decreases the detection limits to low parts per million (ppm) levels. This is crucial, since

many of the fission product elements are present at concentrations below the detection limits of traditional microbeam methods (e.g., electron microprobe). The focused beam of the micro-XRF ($\sim 2 \mu\text{m}^2$) will allow point analysis of the smallest grains, and it will enable the study of alteration and elemental zonation within the larger grains (<250 μm) by using mapping and traverses. Fissionogenic rare-earth elements are of particular interest because of their relatively high production rate on the fission product curve and their usefulness in neutronic calculations. Traditional electron microprobe and ion probe analysis of rare-earth elements is also difficult because of the numerous interferences in the *l* and *m* x-ray emission lines (for x-ray techniques) and mass interferences (for isotopic techniques). However, the high-energy beamline (> 50 keV) available at the APS will make it possible to study the *k*-alpha x-ray emission lines of the rare-earth elements, a novel approach not possible without this beamline.

Results

A preliminary study of the Oklo samples done by using the micro-XRF setup at the MHATT-CAT beamline at the APS was completed in 2002 to develop the methods required for a systematic characterization of these samples. More extensive studies using micro-XRF are planned in the future. The micro-XRF data collected at the MHATT-CAT beamline will complement secondary ion mass spectrometry (SIMS) isotopic analyses designed to better constrain reactor zone neutronic parameters. The isotopic analyses will allow us to model the distribution of fission products within the fossil reactors [2]. Micro-XRF data obtained at the beamline will allow us to study the quantitative trace-element distribution at a variety of length scales within a reactor zone. Together, the SIMS and micro-XRF data will allow us to improve our understanding of the retention and migration of fission products across the reactor zone over the past 2 Ga years [2].

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References

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