# THE OXYGEN ISOTOPIC COMPOSITION OF NANO-SCALE URANINITE AT THE OKLO-OKÉLOBONDO NATURAL FISSION REACTORS, GABON

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## Introduction

The oxygen isotopic composition of uranium minerals and their nanostructures are sensitive monitors of fluid events and provide key tools for studying the evolution of the Oklo-Okélobondo and Bangombé uranium deposits. However, the post-criticality evolution of the uraninite is only partially understood because the results from the few studies that have reported oxygen isotopic data present conflicting results (Pourcelot and Gauthier-Lafaye, 1998). The study of uranium deposits is also complicated by the susceptibility of uraninite to alteration and radiation damage (e.g., Fayek et al. 2000; Jensen and Ewing, 2001; Fayek et al., 2002) and because the effects of these processes are most evident at the nano- and μm scale. Oxygen isotope analysis of uraninite on the micrometer scale has been demonstrated using secondary ion mass spectrometry (SIMS) (Fayek et al., 2002), but such measurements have not yet been related to specific nanostructures. Here we present high-resolution transmission electron microscopy (HRTEM) analyses and *in situ* oxygen isotopic data obtained by SIMS of uraninite from natural fission reactors at Oklo-Okélobondo. These results are used to assess the extent of meteoric water interaction with the Oklo-Okélobondo natural fission reactors.

## The Francevillian Uranium Deposits

The Oklo-Okélobondo and Bangombé uranium deposits formed at moderate depths and temperatures (ca.~1-3 km and ~130°C) in response to interaction between uraniferous, oxidizing brines and reducing oil-bearing fluids along the contact between the fractured FA-formation and the relatively impermeable FB-formation (e.g., Parnell, 1996). The fluids that precipitated these uranium deposits had a $\delta^{18}O$ value of +5 ± 1‰ (Gauthier-Lafaye et al., 1989). Based on petrography and isotopic analysis of uraninite and minerals associated with uraninite (e.g., Michaud and Mathieu, 1998; Jensen and Ewing, 2001), there are at lease three stages of uraninite, and secondary uranium minerals such as coffinite, which are associated with supergene alteration and appear late in the paragenesis. Uraninite has a range of macro-textures from idiomorphic and brecciated grains to colloform textures, and generally has been subjected to massive lead-loss and alteration to coffinite, uranyl silicates, uranyl-hydroxy sulphates and uranyl oxide hydrates with recrystallization and vein formation occurring at the μm-scale (e.g., Jensen and Ewing, 2000, 2001.

At present, the natural fission reactors at Oklo and Okélobondo occur over a range of depths (75 to 400 m) and provide a unique opportunity to study the behavior of fluid-uraninite interaction in near surface oxidizing environments and more reducing deep environments similar to radioactive waste repository conditions (Fig. 1a). Given the size of the uranium minerals (~10 μm-1 cm), we utilized secondary ion mass spectrometry (SIMS) to obtain *in situ* oxygen isotope analyses from discreet regions at the scale of ~15 μm. Areas analyzed by SIMS were then examined by high-resolution transmission electron microscopy (HRTEM) and analytical electron microscopy (AEM) to characterize the nanotextures associated with distinct oxygen isotopic compositions of uraninite. Selected area electron diffraction (SAED) patterns were acquired using a constant size selected aperture so that the size distribution of the uraninite nano-domains can be inferred. Bright-field scanning transmission electron microscopy (BF-STEM) was used to obtain distribution maps of Si and U at the nano-scale.

**SIMS Mapping of $\delta^{18}O$ Variation in Uraninite**

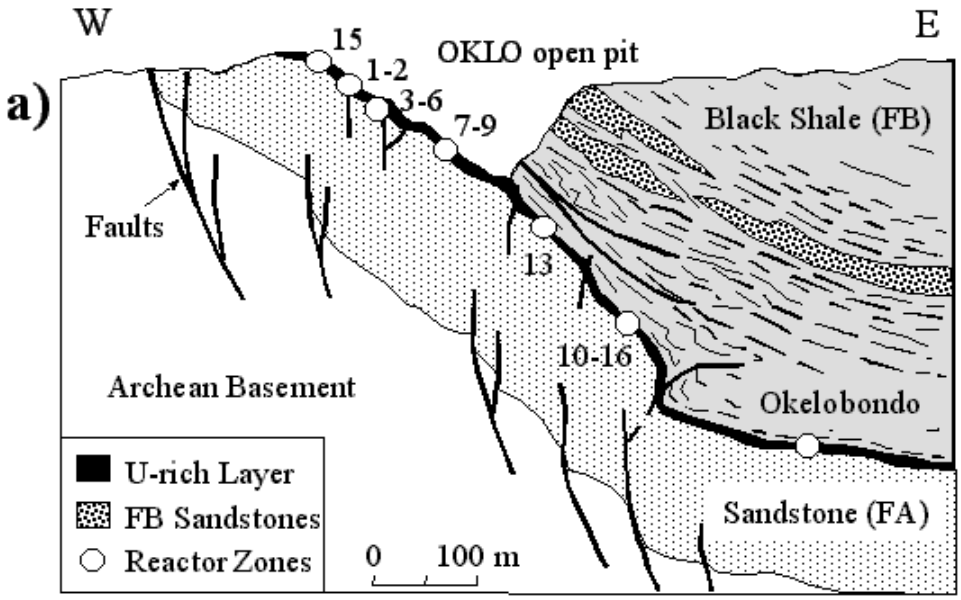
Pourcelot and Gauthier-Lafaye (1998) sampled uraninite from Oklo and Okélobondo natural fission reactors over a range of depths from surface outcrops to 450 m. They reported $\delta^{18}O$ values for uraninite ranging from –13.0‰ to –0.2‰, but did not observe any correlation with depth. The potential cause of difficulty in interpreting conventional oxygen isotopic measurements from uraninite is that the relatively large sample (>5 mg) required to obtain sufficient material for analysis greatly exceeds the scale of textural variation. To minimize such effects, we have used SIMS to measure the $\delta^{18}O$ values of discrete zones in uraninite from reactors that occur over a range of depths (75 to 400 m). Uraninite from shallow reactors (RZ 2, 9) has the lowest $\delta^{18}O$ values (-14.4‰ to -8.5‰) relative to uraninite in reactors located at greater depths (RZ 10, 13, Okélobondo), which has $\delta^{18}O$ values from -10.2‰ to -5.6‰ (Fig. 1b). Variation in uraninite-$H_2O$ oxygen isotope fraction as a function of temperature is <2‰ between 50-300°C (e.g., Fayek and Kyser, 2000). Therefore, the $\delta^{18}O$ values in uraninites from the deepest reactor zones suggest that these uraninites have precipitated from fluids with $\delta^{18}O$ values of ca. +6 ± 1‰. Such a composition is similar to the fluids that were in equilibrium with phyllosilicates associated with these reactors (ca. +5 ± 1‰; Gauthier-Lafaye et al., 1989). However, the observed $\delta^{18}O$ values in the uraninites from the shallowest reactor zone (RZ2) suggest that these uraninites have interacted with or precipitated from fluids with $\delta^{18}O$ values of ca. -4‰. This composition is similar to present-day meteoric water (-4‰; Louvat et al., 1995). Thus recent re-equilibration of oxygen isotopes within uraninite is more extensive in shallow reactors than in those located at greater depths.

Samples in this study from RZ9 contained abundant coffinite. Although efforts were made to avoid Si-rich areas, Si was present at the nanoscale (see below) and therefore was unavoidable. Consequently, the heaviest $\delta^{18}O$ values were obtained from these samples (Fig. 1b) as is expected from the incorporation of relatively $^{18}O$-rich $SiO_2$ during alteration of uraninite (Fayek and Kyser, 1997; Fayek et al., 2000). However, bulk oxygen isotopic analysis of a pristine uraninite sample from RZ9 gave a $\delta^{18}O$ value of –13.0‰ (Pourcelot and Gauthier-Lafaye, 1998). These results show that recent meteoric fluids overprinted the oxygen isotopic composition of uraninite from RZ9 whereas some uraninites were chemically altered to coffinite.

**Nanotextures**

The SAED patterns and HRTEM images from the same samples analyzed by SIMS are shown in Figure 2 in the order of increasing depth from (a) to (e). Uraninite grains from reactors near the surface (e.g., RZ 2 and 9), which have $\delta^{18}O$ values (-14.4‰ to -8.5‰) consistent with interaction with meteoric water, consists of nano- to micrometer size crystallites (Fig. 2a,b). The SAED patterns reveal concentric streaking of diffraction spots, which is caused by the large-angle grain boundaries between the uraninite crystallites. In contrast, SAED patterns and HRTEM images of uraninite from reactor zones that occur at depth (Figs. 2 c, d, e), which have largely retained their original $\delta^{18}O$ values (-10.2‰ to -5.6‰), show that these samples are crystalline and essentially defect-free (Fig. 2c, d, e).

Since oxygen diffusion in uraninite is a relatively fast process, at low temperatures (Fayek and Kyser, 2000), oxygen isotope exchange occurs between the uraninite nanocrystallites and fluids; thus overprinting the original oxygen isotopic composition of the uraninite. These results emphasize the importance of using *in situ* high spatial resolution analysis techniques (SIMS combined with HRTEM) to fully characterize the interactions and alteration of solids in contact with fluids. At Oklo-Okélobondo, meteoric water is interacting with the shallower reactor zones, which is evident from the oxygen isotopic analyses (Fig. 1) and the nanotextures of the uraninite (Fig. 2).



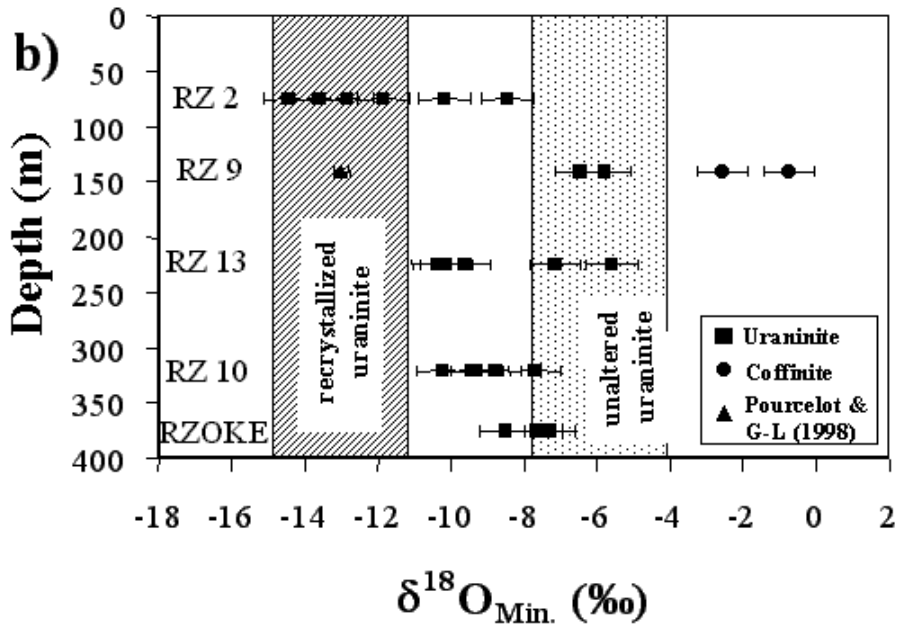




Figure 1. (a) The location of the Oklo-Okélobondo reactor zones (RZ) projected on a cross-sectional plane (from Pourcelot and Gauthier-Lafaye, 1998); (b) *In situ* SIMS oxygen isotope analyses of uraninite and coffinite from each reactor zone. Uranium minerals from reactor zones nearest to the surface have the largest variation in their $\delta^{18}O$ values, and plot within the recrystallized uraninite field, whereas uraninite from reactor zones at depth have retained their original $\delta^{18}O$ values.

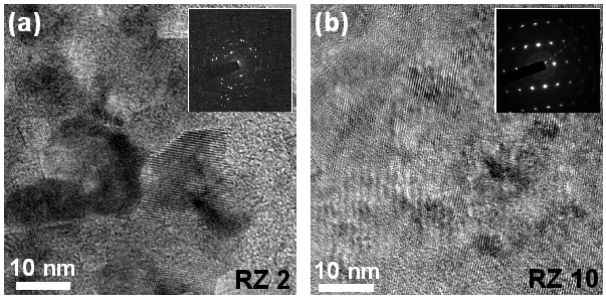



Figure 2. High-resolution transmission electron microscopy (HRTEM) images with selected area diffraction pattern (inset) of uraninite from (a) reactor zone (RZ) 2 (depth from surface 75 m) with $\delta^{18}O$ values from -14.4‰ to -8.5‰; (b) reactor zone (RZ) 10 (depth from surface 320 m) with $\delta^{18}O$ values from -10.2‰ to -7.7‰. Note that the sample from shallow reactor zone RZ2 shows a polycrystalline nanotexture, whereas the sample from the deeper reactor zone RZ 10 shows very few defects.

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