

Oxygen isotope fractionation among uranium oxides: a tracer of origins and transformations of nuclear material

M.DIERICK^{1*}, E.PILI², S.SZENKNECT³,
P.AGRINIER¹

¹ IGP, 75005 Paris, France

² CEA, DAM, DIF, F-91297 Arpajon, France

³ ICSM, CEA/CNRS/ENSCM, 30207 Bagnols/Cèze, France

*(correspondence: dierick@ipgp.fr)

In order to validate tools for the control of illicit trafficking of nuclear material, we study the fractionation of oxygen isotopes in uranium oxides synthesized at various T - f_{O_2} -pH conditions that mimics three main steps of the front-end of the nuclear fuel cycle: dissolution-precipitation, calcination and reduction. First, a new reliable and precise method for oxygen isotope ratios determination in uranium oxides has been developed [1].

During dissolution with ($H_2SO_4 + Fe$) of pure UO_2 followed by its precipitation as ammonium diuranate ($(NH_4)_2U_2O_7$) or uranium peroxyde ($UO_2 \cdot O_2 \cdot nH_2O$, $0 < n < 4$) using NH_4OH or H_2O_2 respectively, the isotope fractionation factor at $50^\circ C$ in the system U_2O_7 - H_2O is between 10 ‰ and 15 ‰, as proposed by [2,3] for UO_3 - H_2O . For the system UO_4 - H_2O the isotope fractionation at $50^\circ C$ is between 20 ‰ and 25 ‰. During calcination ($750^\circ C$, 3h), $(NH_4)_2U_2O_7$ or $UO_2 \cdot O_2 \cdot nH_2O$ are converted into U_3O_8 . The isotope fractionation in the system U_3O_8 - O_2 at $750^\circ C$ is around -16 ‰ for the calcination of $(NH_4)_2U_2O_7$ and between -46 ‰ to -86 ‰ for the calcination of $UO_2 \cdot O_2 \cdot nH_2O$. This shows an unexpected preferential loss of ^{18}O , in disagreement with isotope equilibrium [4] and kinetic isotope fractionation. In opposition, reduction ($850^\circ C$, 2h, Ar- H_2) that converts U_3O_8 into UO_2 , leads to a preferential loss of ^{16}O . The isotope fractionation in the system UO_2 - O_2 is around 22 ‰ for iron free pathways, and between 42 ‰ and 72 ‰ for the others.

These new constraints on the systems U_2O_7 - H_2O , UO_4 - H_2O , U_3O_8 - O_2 and UO_2 - O_2 show that each step of the synthesis pathways mark the produced uranium oxides due to specific and large oxygen isotope fractionations. Large variations in binding energies of oxygen with uranium in the various products is a key parameters to understand these fractionations. Oxygen isotopes are therefore a tool to investigate industrial history of uranium oxides.

[1] Dierick et al. (2016), *Geostand. Geoanal. Res.* [2] Zheng (1991), *GCA* **55**, 2299-2307. [3] Fayek and Kyser (2000), *GCA* **64**, 2185-2197 [4] Plaue (2013), Ph.D Dissertation.