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Analysis of a Uranium-Rich Sample Interdicted in Durban, South Africa (FSC 14-1-1)

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Disclaimer

Auspices Statement

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Abstract

We provide a summary of the analyses of a 1 kg uranium ore concentrate sample seized in Durban, South Africa on 19 November 2013. Results are presented for compound identification, morphology, U assay, Sr, Pb and U isotope composition and age. The sample is a fine-grained mixture of two common uranium compounds – ammonium uranyl fluoride and a hydrated uranium-ammonium oxide. The uranium isotope composition indicates the material is depleted in ^{235}U relative to natural uranium consistent with the initial NDA measurements performed by the Nuclear Energy Corporation of South Africa (NECSA). A comparison of the data for this sample with data in the Uranium Sourcing Database failed to find a match, indicating the sample was not produced at a facility represented in the database. Calculations of the performance of a graphite moderated reactor using natural uranium fuel suggest the characteristics of the Durban sample are consistent with fuel irradiated to a burn-up of 1.6 GWD/MTU and then used as the feedstock for an enrichment cascade producing uranium enriched in ^{235}U to between 2 and 10%.

Introduction

This report documents the analysis of a 1 kg uranium-rich sample seized by South African police in a sting operation in Durban, South Africa on 19 November 2013. The sample was initially analyzed by NECSA using non-destructive methods and determined to have an isotopic composition depleted in ^{235}U with a ^{235}U abundance of 0.32% compared to a value of 0.72% for natural uranium. In December 2013, the U.S. State Department and the South African Department of International Relations and Co-operatives organized transport of a ~10g aliquot of the sample to Lawrence Livermore National Laboratory (LLNL) on for a comprehensive nuclear forensic analysis. The results of these analyses are presented herein.

Analytical Methods

Shortly after the sample was received, the entire sample was transferred to a plastic container and analyzed in the LLNL gamma-ray counting facility for 5 days. Following this analysis, approximately 1g was removed for analysis and split into aliquots. The analytical procedure began with XRD analyses, followed by analyses for compound identification, morphology and U isotopes. Additional analyses of U concentration, trace element abundances, Pu isotopes and age are currently underway.

The phase composition was determined by X-ray diffraction (XRD). The samples were analyzed on a Bruker AXS D8 ADVANCE X-ray diffractometer equipped with a LynxEye 1-dimentional linear Si strip detector; DIFFRACplus Evaluation package Release 2009 software was used for data analysis. Morphology was characterized with an FEI Inspect FE-SEM equipped with a Kevex EDS x-ray system. A visible/NIR spectrometer (Analytical Spectral Devices, Inc.) equipped with three detectors that spanned consecutive spectral regions: 350 – 1000 nm (Vis+), 1000 – 1800 nm (NIR1), and 1800 – 2500 nm (NIR2) was used for optical spectroscopy. Trace element abundances were measured with a TherData reduction and analysis were performed using the Unscrambler X ver. 10.1 (CAMO Software AS). Trace element abundances were determined using a ThermoScientific ICAP-Q ICP-MS, while the U concentration was measured by Davies-Gray titration. Sr isotope compositions were measured following chemical separation by thermal ionization mass spectrometry (TIMS, ThermoScientific Triton), while Pb, U and Pu isotope composition were measured using mass spectrometry after dissolution in HNO_3/HF using high-resolution multi-collector inductively coupled plasma-mass spectrometry (MC-ICP-MS, Nu Plasma). The age since last chemical reprocessing was determined using the ^{234}U – ^{230}Th chronometer.

Abundances of Radionuclides

Following the 5-day gamma count, the abundances of radionuclides were determined using GAMANAL; results are shown in table 2.

Table 1. Radionuclide abundances in the Durban sample.

Radionuclide	Concentration (at. %)[1]	Concentration (atoms)
^{95}Zr		$<1.23 \times 10^{7}$
^{106}Ru		$<1.85 \times 10^{9}$
^{125}Sb		$<3.69 \times 10^{8}$
^{137}Cs		$<1.85 \times 10^{9}$
^{144}Ce		$<3.69 \times 10^{8}$
^{155}Eu		$<3.69 \times 10^{8}$
^{234}U	$(1.020 \pm 0.20) \times 10^{-3}$	
^{235}U	0.0333 ± 0.001	
^{238}U	99.67 ± 0.20	

1. Uncertainties are 2 standard deviations

Phase composition

The analytical results are shown in Table 1. The analyses demonstrate that the sample is a mixture of ammonium uranyl fluoride plus 2 hydrated uranium-ammonium oxide phases differing in the relative abundances of NH_3 and UO_3.

Table 1 – Analytical X-ray diffraction results for FSC-14-1-1.

Ammonium Uranium Fluoride	$(NH_4)_2UF_6$
Uranium Oxide Ammonia Hydrate	$2UO_3{\cdot}NH_3{\cdot}3H_2O$
Ammonium Uranium Oxide Hydrate	$UO_3{\cdot}NH_3{\cdot}H_2O$
Ammonia Uranium Oxide Hydrate	$UO_3{\cdot}zNH_3{\cdot}xH_2O$

Optical Spectroscopy

The sample is a fine-grained powder as shown in the white light photo in Figure 1.

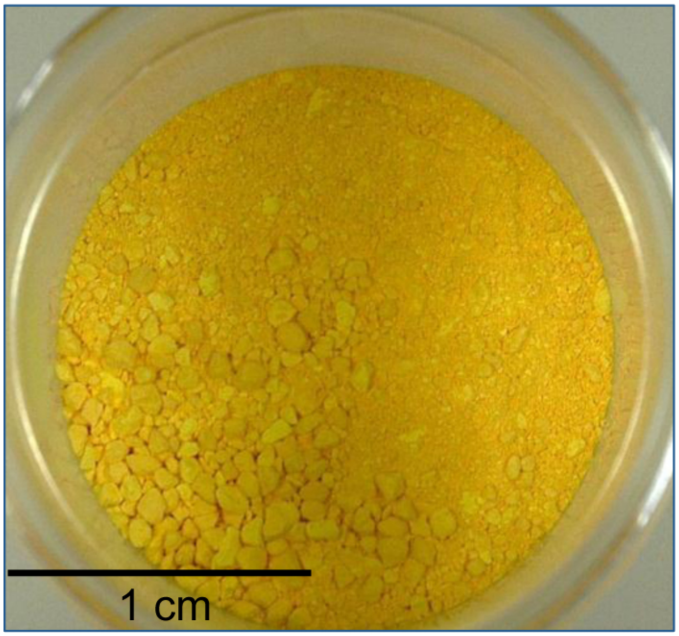

Figure 1. While light photograph of FSC 14-1-1.

Vis/NIR reflectance spectroscopy provided a rapid non-destructive evaluation of the phases present in the Durban sample. The sample appeared to have some inhomogeneity based on visual appearance and this was confirmed with the spectral measurements. The sample appears to have been produced by the NH_3 process with a relative low drying temperature of between 85° and 150° C. Some of the lighter colored particles may have experienced a different temperature than the bulk. These particles could have come from a different location in the furnace or from a different batch but do appear to have come from the same process. Based on a comparison of the spectra to other samples in the Uranium Sourcing Database, the material is primarily an ammonium uranate with the general formula of $(NH_4)_2U_2O_7$, $UO_3{\cdot}xH_2O{\cdot}yNH_3$, or $UO_2(OH)_2{\cdot}xH_2O{\cdot}yNH_3$.

Morphology

SEM/EDS examination reveals the sample is composed of a fine-grained aggregate of tabular to anhedral grains raging in size from <0.2 to 1 μm; thin platelets are particularly abundant. The individual grains are self-assembled into aggregates ~50 to 500 μm in diameter. No correlation between chemical composition and morphology was observed. A number of small aggregates 5-10 mm in size, composed of multiple fine grains are present (Figs. 2, 3).

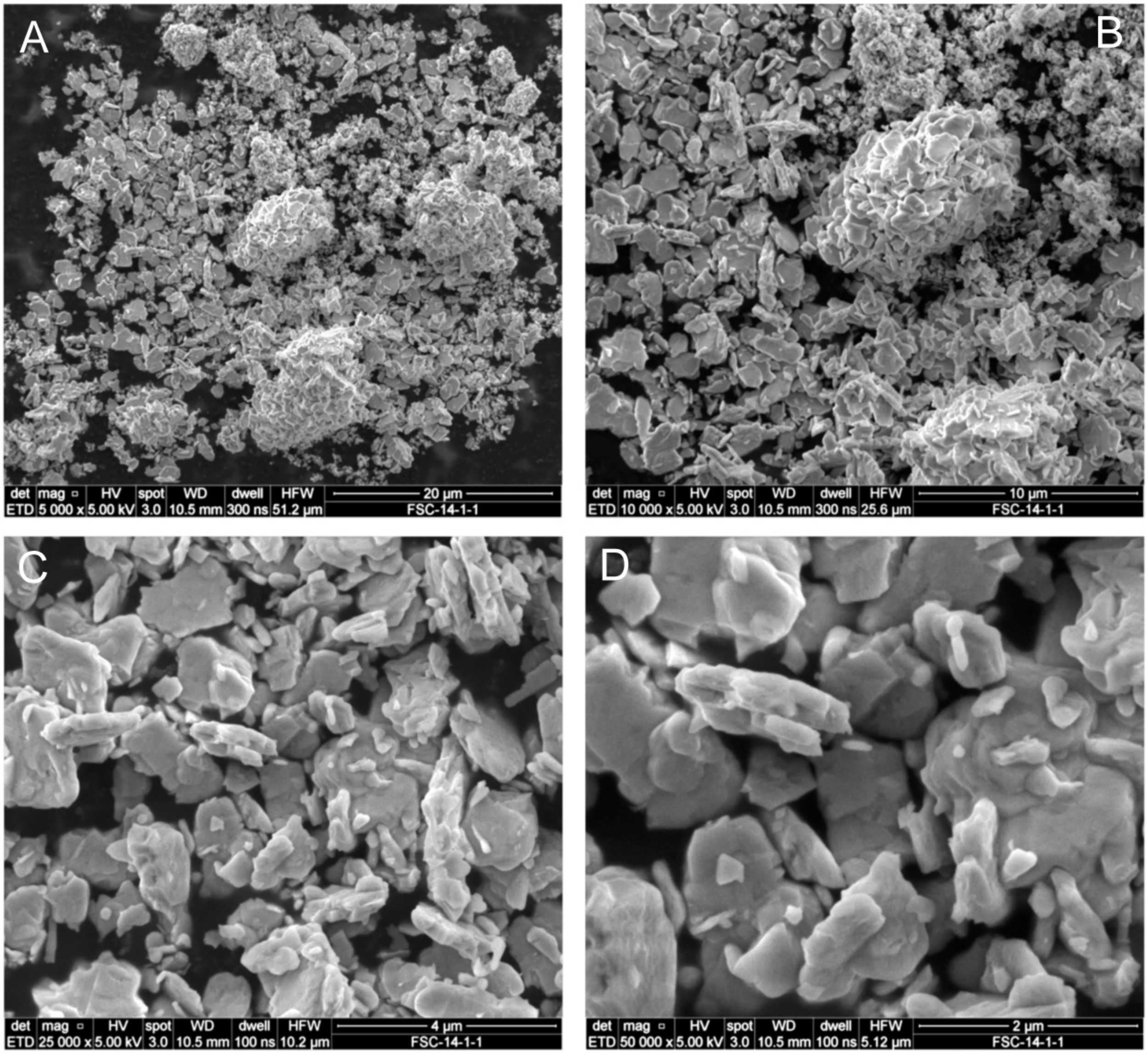

Fig. 2. SEM secondary electron photomicrographs showing characteristic morphologies of FSC 14-1-1. (A) Dispersed particles; scale bar is 20 µm. (B) Close up of aggregate composed of dispersed individual grains and clumps of grains; scale bar is 10 µm. (C, D); Close-up views o individual grains showing varied morphologies; scale bars are 4 and 2 µm, respectively.

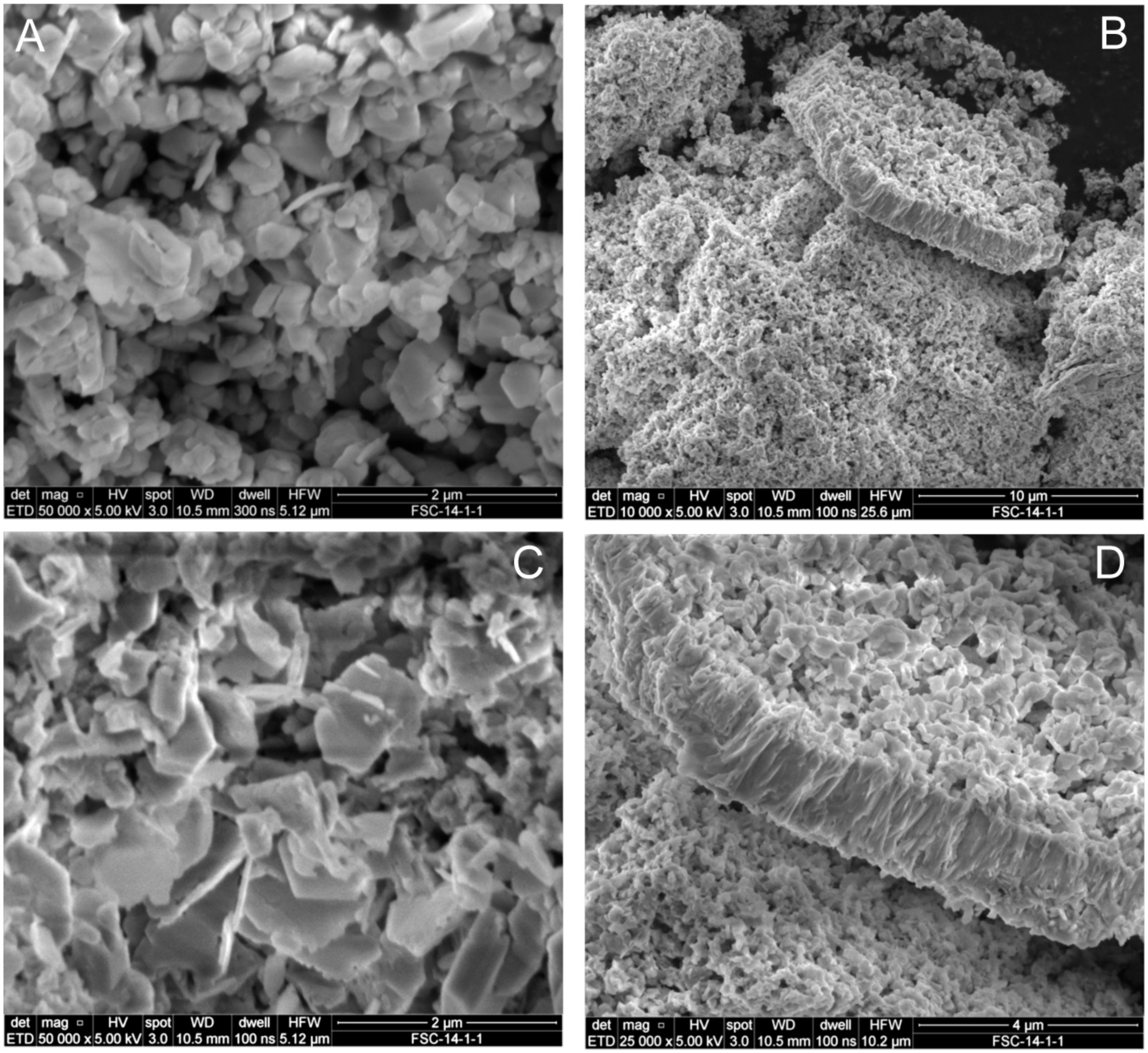

Fig. 3. SEM secondary electron photomicrographs showing characteristic morphologies of FSC 14-1-1. (A) Dispersed particles; scale bar is 2 μm. (B, D) Views of platelets composed of particle aggregates; scale bars are 10 and 4μm, respectively; (C) Close-up views of top surface of platelet shown in (B). Individual grains exhibiting varied morphologies are apparent; scale bar is 2 μm.

Trace Element Abundances and U Assay

Trace elements abundances and U content were determined on separate aliquots of the dissolved sample; results are summarized in table 2.

Table 2. Trace element abundances and U content

Element	Technique	unit	Avg. (n=3)	Uncertainty	Lc[1,2]
Be	ICP-MS	µg/g	0.008	0.004	0.0025
B	ICP-MS	µg/g	3	8	0.42
Na	ICP-MS	µg/g	34.4	1.8	9
Mg	ICP-MS	µg/g	1.3	1.3	0.6
Al	ICP-MS	µg/g	8	2	1.2
Si	XRF	µg/g	<270		267
P	XRF	µg/g	<200		200
S	XRF	µg/g	<175		172
Cl	XRF	µg/g	<125		123
K	ICP-MS	µg/g	90	30	14
Ca	ICP-MS	µg/g	38	14	30
Sc	ICP-MS	µg/g	0.28	0.16	0.026
Ti	ICP-MS	µg/g	0.9	0.2	0.21
V	ICP-MS	µg/g	0.23	0.03	0.0022
Cr	ICP-MS	µg/g	8	3	0.2
Mn	ICP-MS	µg/g	0.8	0.2	0.019
Fe	ICP-MS	µg/g	100	30	3.3
Co	ICP-MS	µg/g	0.36	0.04	0.002
Ni	ICP-MS	µg/g	3	2	0.1
Cu	ICP-MS	µg/g	0.78	0.16	0.05
Zn	ICP-MS	µg/g	2.8	1.8	0.7
Ga	ICP-MS	µg/g	0.009	0.002	0.00061
Ge	ICP-MS	µg/g	0.023	0.02	0.005
As	ICP-MS	µg/g	0.55	0.04	0.0016
Se	ICP-MS	µg/g	12	0.5	0.4
Br	XRF	µg/g	<80		80
Rb	ICP-MS	µg/g	0.088	0.005	0.014
Sr	ICP-MS	µg/g	0.27	0.05	0.04
Y	ICP-MS	µg/g	0.0026	0.0005	0.00022
Zr	ICP-MS	µg/g	0.11	0.06	0.008
Nb	ICP-MS	µg/g	0.113	0.009	0.00029
Mo	ICP-MS	µg/g	18.8	0.9	0.01
Ru	ICP-MS	µg/g	0.0007	0.0009	0.00022
Rh	ICP-MS	µg/g	0.00028	0.00015	0.00011
Pd	ICP-MS	µg/g	0.0011	0.001	0.0003
Ag	ICP-MS	µg/g	0.23	0.03	0.006
Cd	ICP-MS	µg/g	3.08	0.19	0.0019
Sn	ICP-MS	µg/g	0.49	0.04	0.033
Sb	ICP-MS	µg/g	2.12	0.14	0.003
Te	ICP-MS	µg/g	0.86	0.13	0.006
Cs	ICP-MS	µg/g	156	12	0.0041

Ba	ICP-MS	µg/g	3	0.2	0.04
La	ICP-MS	µg/g	8.9	0.5	0.0028
Ce	ICP-MS	µg/g	0.061	0.003	0.0004
Pr	ICP-MS	µg/g	0.0017	0.0006	0.00009
Nd	ICP-MS	µg/g	0.005	0.002	0.00023
Sm	ICP-MS	µg/g	0.0012	0.0007	0.00038
Eu	ICP-MS	µg/g	0.0005	0.00016	0.00008
Gd	ICP-MS	µg/g	0.0021	0.0006	0.00033
Tb	ICP-MS	µg/g	0.00006	0.00018	0.000034
Dy	ICP-MS	µg/g	0.0005	0.0007	0.0001
Ho	ICP-MS	µg/g	0.00014	0.00008	0.000038
Er	ICP-MS	µg/g	0.0005	0.0005	0.00016
Tm	ICP-MS	µg/g	0.00011	0.00006	0.000019
Yb	ICP-MS	µg/g	0.0005	0.0003	0.00013
Lu	ICP-MS	µg/g	0.00012	0.00006	0.000025
Hf	ICP-MS	µg/g	0.0017	0.0013	0.00054
Ta	ICP-MS	µg/g	0.0009	0.0005	0.00007
W	ICP-MS	µg/g	0.22	0.02	0.0015
Re	ICP-MS	µg/g	0.0005	0.0002	0.000208
Ir	ICP-MS	µg/g	0.0003	0.0005	0.0003
Pt	ICP-MS	µg/g	0.0004	0.0007	0.0003
Tl	ICP-MS	µg/g	0.298	0.015	0.00021
Pb	ICP-MS	µg/g	7.6	0.5	0.007
Bi	ICP-MS	µg/g	0.12	0.02	0.03
Th	MC-ICP-MS	µg/g	0.170	0.018	0.0006
U	D-G	g/g %	74.9	0.5	

[1] Limit of detection

[2] The units of the Lc values correspond to column 2.

Sr, Pb, U and Pu Isotope compositions and Age

The Pb, U and Pu isotope compositions were determined by MC-ICP-MS on chemically purified aliquots of the sample; Sr isotopes were determined by TIMS. The data are shown in tables 3-6 and Fig. 4. The uranium isotope composition indicates the Durban material is depleted in ^{235}U compared to natural uranium, while the elevated ^{236}U content indicates the parent material was irradiated in a nuclear reactor. The U-isotope composition of the Durban material was compared to soil samples from Site 300, where the U.S. conducts explosive tests of materials constructed of depleted uranium. The composition of the Site 300 soils represents mixing between U.S. depleted uranium and natural uranium (Esser et al., 2002); no match was found. The Sr and Pb isotope compositions are depicted in an isotope correlation diagram (Fig. 4). The data confirm the absence of a match with any UOC samples contained in the U-Sourcing Database. The time since the sample was last chemically processed (model age) was determined using the ^{234}U – ^{230}Th chronometer; the age is 30.9 ± 0.4 years, corresponding to a production date of 30 April 1982 with an uncertainty of 130 days. The model age assumes complete separation of Th and U during chemical processing and represents an upper limit to the actual time of production.

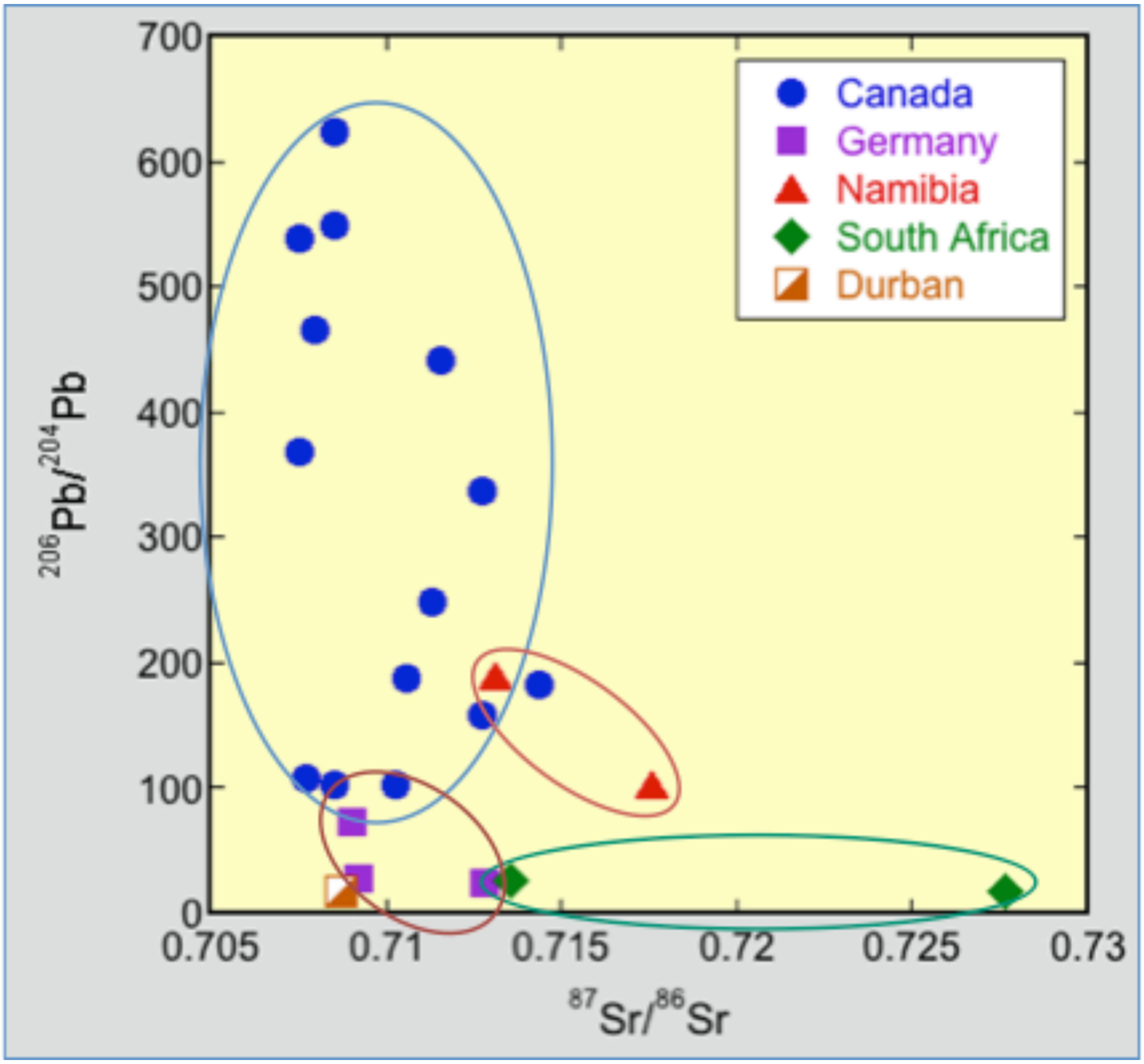

Fig. 4. Isotope correlation diagram showing Sr and Pb isotope compositions of the Durban UOC compared to UOC from Germany, Namibia, South Africa and Canada; data for these UOC samples are taken from the Uranium Sourcing Database (Robel et al., 2012). The lack of a match for the source of the Durban UOC with UOC from the database is apparent.

Table 3. U Isotope Composition

U Isotope	Abundance (at.%)	Uncertainty
^{234}U	0.0021107	0.0000072
^{235}U	0.31963	0.00024
^{236}U	0.018437	0.000070
^{238}U	99.6639	0.0020

Table 4. Sr Isotope Composition

Sample	$^{87}Sr/^{86}Sr$	2σ	k	$^{84}Sr/^{88}Sr$	2σ	k
FSC-14-1-1-B	0.708699	0.000040	2	0.056536	0.000026	2

Table 5. Pb Isotope Composition

Sample	Pb (ng/g)	$^{208}Pb/^{204}Pb$	2σ	k	$^{207}Pb/^{204}Pb$	2σ	k	$^{206}Pb/^{204}Pb$	2σ	k
FSC-14-1-1-B	552	37.849	0.023	2	15.6088	0.0076	2	18.0630	0.0086	2
FSC-14-1-1-B[1]	676	37.848	0.022	2	15.6090	0.0076	2	18.0633	0.0086	2

[1] Duplicate analysis.

Table 6. Pu Isotope Composition

Sample	Pu (pg/g)	2σ	k	^{240}Pu/^{239}Pu	2σ	k
FSC-14-1-1-B	9.69	0.67	2	0.0719	0.0037	2

The U-isotope composition of the Durban material was compared to soil samples from Sit where the U.S. conducts explosive tests of materials constructed of depleted uraniu composition of the Site 300 soils represents mixing between U.S. depleted uranium and r uranium (Figs. 6, 7; Esser et al., 2002).

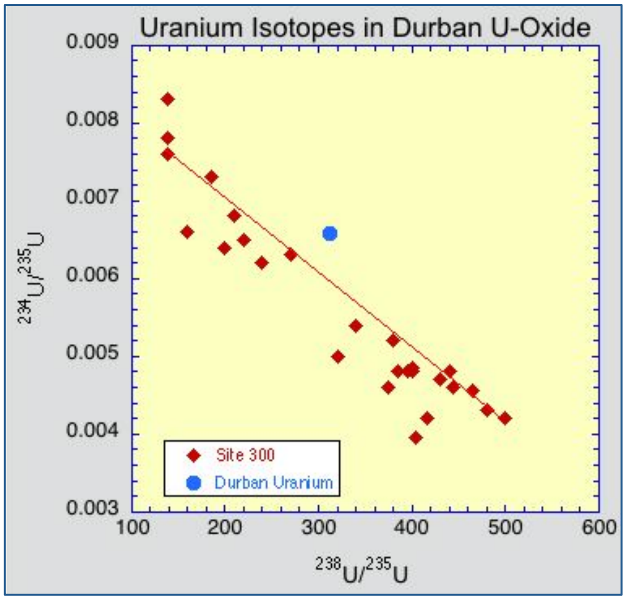

Fig. 6. Uranium 3-isotope plot showing ^{234}U/^{238}U vs. ^{235}U/^{238}U for the Durban sample compared to soils from Site 300 (see text). The ^{234}U/^{238}U of the Durban material is within the range of comparable materials produced in the U.S.

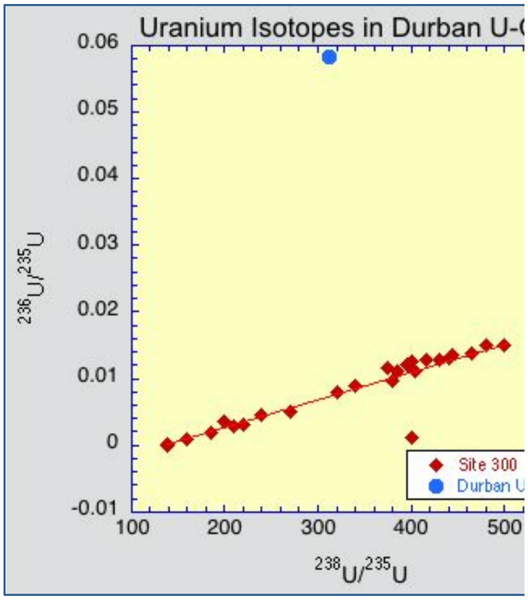

Fig. 7. Uranium 3-isotope plot showing ^{236} vs. ^{235}U/^{238}U for the Durban sample compa soils from Site 300 (see text). The ^{236}U/^{238}U Durban material is substantially higher than of comparable materials produced in the excluding the possibility the material origin the U.S.

Reactor Models

To explore potential sources of the Durban sample, we modeled the performance of a graphite moderated, natural uranium (NU) fueled reactor using the MAGNOX reactor model included in the Origen-ARP component of SCALE 6.1 (Bowman and Cook, 2000). NU fuel irradiated for ~100 days to a burnup of 1.6 GWD/MTU would have a ^{240}Pu content of ~14% at discharge. Using this fuel as feed for an enrichment cascade producing ^{235}U enriched to 2%, we used the ORNL MSTAR program to calculate a ^{234}U /^{235}U ratio of 9.1×10^{-3} and a ^{236}U /^{235}U ratio of 4.2×10^{-2}. Both values are in good agreement with the measured U-isotope composition of the Durban sample. Increasing the enrichment in ^{235}U in the above calculation to 10% also yields a ^{236}U/^{234}U within the measurement uncertainty, predicting a ^{235}U abundance that is ~5% low.

Summary

The sample interdicted in Durban, South Africa is uranium oxide, ammonium uranyl fluoride plus two hydrated uranium-ammonium oxide phases differing in the relative abundances of NH_3 and UO_3. A comparison of the properties of the Durban uranium oxide with samples contained in the Uranium Sourcing Database using principal components analysis, partial least squares derivative analysis and the *iDAVE* search engine failed to produce a match, suggesting the material was produced at a facility that is not represented in the database. We modeled the performance of a Soviet design RBMK reactor using *Origen-S*, an updated version of the *Origen* code with flexible dimensioning and free-form input processing. The RBMK is a graphite-moderated reactor using natural uranium fuel (NU). NU fuel irradiated for ~100 days to a burnup of 1.6 GWD/MTU would have a ^{240}Pu content of ~14% at discharge. Using this fuel as feed for an enrichment cascade producing ^{235}U enriched to 2%, we used the ORNL MSTAR program to calculate a ^{234}U /^{235}U ratio of 9.1×10^{-3} and a ^{236}U /^{235}U ratio of 4.2×10^{-2}. Both values are in good agreement with the measurement of the U-isotope composition of the Durban sample. Increasing the enrichment in ^{235}U in the above calculation to 10% also yields a ^{236}U/^{234}U within the measurement uncertainty, predicting a ^{235}U abundance ~5% low.

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