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Technical Report on the Behavior of Trace Elements, Stable Isotopes, and Radiogenic Isotopes During the Processing of Uranium Ore to Uranium Ore Concentrate

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July 9, 2015

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Auspices Statement

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Current Status:

Geochemical analysis of three sample suites, comprised of two paired uranium ore/uranium ore concentrates (UOC) sets and one suite of U ore, UOC, and intermediate products, has been completed. The sample suites represent three geologic settings, three mining techniques, and three processing techniques, and therefore represent a reasonable cross section of the state of global U mining and concentration. None of the samples were previously included in the Uranium Sourcing Database, and all of the sites are currently producing uranium.

Potential Issues:

None

Project Goals:

The goals of this SP-1 effort were to understand how isotopic and elemental signatures behave during mining, milling, and concentration and to identify analytes that might preserve geologic signatures of the protolith ores. The impurities that are preserved through the concentration process could provide useful forensic signatures and perhaps prove diagnostic of sample origin.

Approach:

In order to assess the behavior of isotopic and elemental signatures during processing, three sets of samples were acquired and analyzed for a variety of geochemical signatures. The sample suites included a paired uranium ore cuttings sample and uranium ore concentrate sample from the Palangana ISR mine and Hobson Processing facility in Texas USA; a paired ore and ore concentrate sample from Denison Mines, and a suite of samples from NUFCOR in South Africa. The NUFCOR samples included a comminuted ore, plus samples of intermediate products and reagents from processing, and finally three uranium ore concentrate samples. A detailed description of the three sample sets follows.

Samples:

Palangana/Hobson:
The Palangana/Hobson samples include drill cuttings from the mineralized zone of an exploration drill hole from the Palangana mine and UOC produced from the section of the mine sampled in the drill hole and produced at the Hobson processing plant. A description of the ore deposit and uranium recovery details follows.

The Palangana Uranium mine is located 25 miles west of the town of Alice, Texas, and 15 miles southeast of Freer, Texas in Duval County. The uranium deposits at Palanagana are contained within fault-controlled roll-fronts in the Pliocene-age Goliad Formation on the flank of the Planagana salt dome. The uranium mineralization occurs at a depth of approximately 25-135 meters below the surface. The uranium mineralization is hosted in four fluvial deposited sand horizons with an average mineralization thickness is 4.5m. The average U grade is 0.036% U_3O_8, but ranges from essentially zero up to ~1% U_3O_8. The mineralization is extremely fine grained, and no specific mineral phase has been identified in the literature. The uranium occurs as a coating on sand grains. The host sands are well-sorted and well-rounded and are composed of quartz, chert, with trace amounts of limestone, volcanic clasts, and kaolinite. Uranium mineralization occurs throughout the sand beds, and although the occurrences are primarily low grade, several high-grade zones have been reported.

Uranium is mined from the Palangana deposit by in-situ recovery (ISR). The process begins by pumping out local groundwater, oxidizing that groundwater, and re-injecting the oxidized groundwater through the uranium bearing sandstone layers. The oxidized groundwater is used for dissolving the uranium coating on the sandstone grains and selectively extracting uranium within the formation. This "pregnant solution" containing the dissolved U is then pumped through an ion exchange column that removes the U from solution. The loaded resin is then pumped into a tanker truck, and transported from the satellite mine to a central processing facility at Hobson, Texas. Once at the Hobson processing facility, the loaded resin is pumped into an elution column, and the uranium is stripped from the resin with a sodium carbonate eluent solution. The stripped ion exchange resin is then pumped back into a truck and returned to the mine site for re-use. Uranium is complexed with carbonate in the eluent, which is then transferred to a precipitation tank. Uranium is precipitated from the eluent solution with HCl and H_2O_2. Following precipitation, the uranyl slurry is passed through a filter press and the uranyl product is rinsed with neutral pH water. Finally the product is dried in a vacuum dryer and loaded into drums. The product is not calcined.

Denison/Denison "Dirt"

The Denison samples appear to be sourced from the McClean Lake deposit in Canada, although the precise origin of the samples is not clear. Nevertheless, the sample set consists of a paired ore and uranium ore concentrate from the same deposit. A description of the ore deposit and uranium recovery details from McClean Lake facility follows.

The McClean Lake site includes several uranium deposits located on the eastern edge of the Athabasca Basin in northern Saskatchewan, approximately 26 km west of the Rabbit Lake mine, and 250 km north of Saskatoon. The McClean Lake deposits include the JEB, McClean, Sue, and Caribou deposits, plus several exploration prospects that have yet to be mined. Production of UOC from the McClean Lake deposits began in 1999. The bedrock geology of the area consists of Precambrian gneisses unconformably overlain by flat lying, unmetamorphosed sandstones and conglomerates of the Athabasca Group. The mineralized zones in the McClean Lake deposits occur as sausage shaped pods straddling the unconformity between the Athabasca sandstones and the crystalline basement. The high-grade section of the mineralized pod undulates from 13 m above to 13 m below the unconformity contact, which averages 160 m below the ground surface. The uranium is hosted in altered sandstones and basement rocks. The alteration is characterized by hematitically altered clay-rich zones. Illite is the predominant clay which forms massive layers. Uranium occurs as fine-grained coffinite, in veinlets and nodules of pitchblende, as well as in massive patches of pitchblende/uraninite. Typical ore grades are up to 2.4% U_3O_8, though ore produced in the 2006-2010 were significantly lower grade. Small amounts of nickel arsenides are commonly associated with the uranium.

Open pit methods were used to extract U from the McClean Lake mines. The ore rock is either stockpiled or delivered to the onsite McClean Lake Mill. This facility has been designed to process high-grade ore without dilution, and as a result, lower grade or is stockpiled and subsequently processed on an ad-hoc basis. Ore received at the mill is ground using conventional crushing/grinding equipment. The comminuted ore is mixed with water and discharged to air-agitated storage tanks. Uranium is extracted from the ore by chemical dissolution. Oxygen and hydrogen peroxide oxidize the uranium mineralization into a soluble form, and sulfuric acid is used to dissolve the oxidized uranium. The leach discharge slurry is washed and passed through a series of thickeners to separate the uranium solution from waste solids (counter-current decantation). The waste solids are then sent to the tailings circuit. The uranium bearing solution is processed through a clarifier to further reduce the concentration of suspended solids in the solution prior to its introduction into the solvent extraction circuit. Uranium is extracted using an organic solution of tertiary amines, and then stripped from this solution with ammonium sulfate. Uranium is precipitated as ammonium diuranate, and then thickened prior to drying and calcining. The product is calcined at 800°C prior to packaging.

NUFCOR-South Africa Samples

The NUFCOR sample suite consists of a series of uranium ore, UOC, and intermediate products from the uranium processing circuits at the AngloGold-Ashanti South Uranium Plant near Klerksdorm, North West and the NUFCOR Plant near Westonaria, Gauteng. The sample suite includes a total of 12 discrete samples. A description of each of the samples and the sample processing follows, and is illustrated in Figure 1.

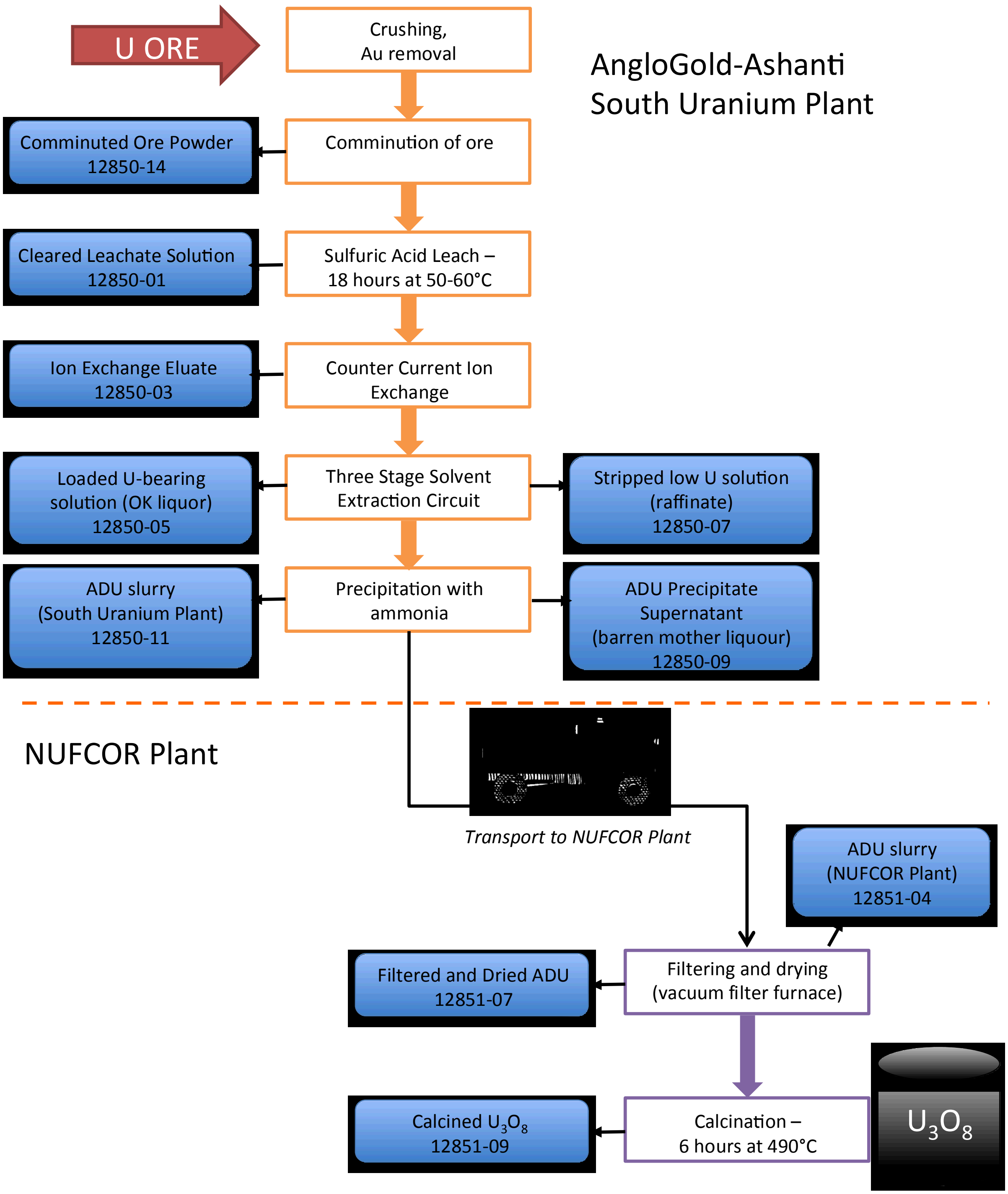

Figure 1 Schematic depiction of sampling at the AngloGold-Ashanti South Uranium Plant and NUFCOR Plants. A detailed description of each sample is provided in the text. The flow chart shows the processing steps from run of mine ore to the final U_3O_8 product, and indicates where in the processing circuit samples were collected. Samples descriptions and sample numbers are included in the blue boxes.

The ore samples are from the Vaal Reef deposits in the Witwatersrand Basin, and represent ore from Kopanang, Great Noligwa, and Moab Khotsong mines. Uranium is hosted in uraniferous quartz-pebble conglomerates of the 2500 to 2800 million years old Proterozoic Witwatersrand Supergroup (Saager et al., 1982). Uranium is recovered from these mines as a byproduct of gold extraction, and gold is always removed from the ore prior to processing for uranium recovery. Uranium occurs as detrital uraninite grains, but trace brannerite and uraniferous leucoxene are also sometimes present in these deposits. Uranium grade varies in these deposits from approximately 0.04-0.05 wt% U_3O_8. The Kopanang, Great Noligwa, and Moab Khotsong mines are underground mines so that ore is extracted by conventional hard rock techniques. The mine product is a comminuted quartzitic gold ore. Prior to entering the uranium extraction circuit at the South Uraniumb Plant, the ore is milled to a powder and the gold is extracted by mechanical separation. The comminuted ore enters the South Uranium Plant as a thick slurry suspended in water. The ore from the three mines is well mixed at this point, obfuscating geochemical signatures of the individual mines. The first sample of this suite is an aliquot of the comminuted ore powder representative of the currently processed material (Sample 12850-14).

The comminuted ore slurry is then leached in sulfuric acid to remove the uranium as well as other metals present. The leaching conditions are 18 hours at 50-60°C. The leach discharge slurry is passed through a series of thickeners to separate the uranium solution from waste solids (counter-current decantation). A sample of the cleared leachate solution (including some recycled raffinate from the solvent extraction circuit) is Sample 12850-01. Following thickening, the cleared leachate solution is passed through a fluidized counter-current ion exchange circuit. The CCIX circuit uses Ambersep 400 SO_4 strong base anion resin designed for uranium recovery. Uranium is eluted in 12% sulfuric acid. Sample 12850-03 is an aliquot of this ion exchange eluate.

The ion exchange eluate is next passed through a three-stage solvent extraction circuit. Uranium is extracted from the eluate by the organic acid Alamine 336, and then stripped with ammonium sulfate. Sample 12850-05 is an aliquot of the uranium bearing ammonium sulfate liquid (also called the OK liquor). Sample 12850-07 is the stripped, low U concentration, solution (raffinate).

Following solvent extraction, uranium is precipitated with ammonia forming an ammonium diuranate (ADU) slurry. The ADU slurry was collected as Sample 12850-11. An additional sample of the supernatant (the barren mother liquour) was collected as Sample 12850-09. The ADU slurry is then transported from the South Uranium Plant to the NUFCOR plant near Westonaria, Gauteng. The ADU slurry is passed through a filtration circuit. Sampling at the NUFCOR plant began with the collection of the feed ADU slurry 12851-04. The slurry is passed through a rotating vacuum filter furnace and dried to ADU powder (Sample 12851-07). Finally, the ADU powder is calcined at 490°C for 6 hours to U_3O_8 powder (Sample 12851-01).

Initial Sample Characterization Results:

The sampling and analysis plan for the three samples was designed to characterize the compounds comprising each sample, as well as their bulk isotopic and trace element compositions. Solid samples were photographed upon receipt, and subsamples were then powdered for X-ray diffraction and microscopy. Powdered aliquots were then dissolved and used for destructive trace element analysis by quadrupole ICP-MS, U assay, and finally U, Pb, Sr, C, N, H, and S isotopic measurements. The liquid samples were only analyzed for trace elements and isotopes.

Table 1 Sample Analysis Plan

Analytical Technique	Measured Parameter
Optical imaging	Physical characterization and morphology
Electron microscopy (SEM/EDS)	Particle size; microstructure and elemental composition
XRD	Crystallographic phase composition
XRF	Trace elements
Davies Gray Titration	U assay for UOC
Quadrupole ICP-MS	Trace elements; U Assay for ores and solutions
MC-ICP-MS	U isotopic analysis; age determination; Sr and Pb isotopic analysis
Elemental Analyzer	Stable isotopes and abundance of C, N, O, and S

X-ray diffraction:

Powdered samples were analyzed on a Bruker AXS D8 ADVANCE X-ray diffractometer equipped with a LynxEye 1-dimentional linear Si strip detector. Bruker DIFFRAC.EVA V3.1 was used for data analysis. Homogenized and crushed samples were analyzed as powder mounts. The samples were scanned from 10 to 70° 2θ. The step scan parameters were 0.02° step and 4 second counting time per step with a 12mm variable divergence slit. The samples were X-rayed with Ni-filter Cu radiation from a sealed tube operated at 40kV and 40mA. An X-ray reference material (Bruker supplied Al_2O_3) was analyzed with the sample to ensure goniometer alignment. No peak shift in the standard scan was observed when the sample was analyzed. Phases in the unknown sample were identified by comparison of observed peaks to those in the International Centre for Diffraction Data (ICDD PDF-2 2009 and PDF-4+ 2013) powder diffraction databases.

Results from XRD analysis are presented in Table 2. Analysis of sample the Palangana Ore indicate that the sample is composed of quartz, dolomite (Mg, Ca)CO_3, and Na-feldspar. This is consistent with the arkosic sandstones, mudstones and claystones of the Goliad formation. The associated UOC, processed at the Hobson Plant, is uranyl peroxide.

Analysis of sample the Denison "Dirt" Ore indicate that the sample is composed of quartz, dolomite (Mg, Ca)CO_3, kaolinite, and a possible minor U-bearing phase. This is consistent with Athabasca sandstone and conglomerates. The associated UOC, is primarily U_3O_8 with lesser UO_2 component. The composition of the final product indicates that the UOC was calcined.

The comminuted ore sample 12850-14 is composed of quartz, pyrophyllite, chlorite, and muscovite. This is consistent with the quartzitic conglomerate typical of the Vaal Reef deposits. Sample 12850-14 is representative of the feedstock ore that is processed for uranium extraction in the South Uranium and NUFCOR plants, and as such has already had the gold fraction extracted. Sample 12850-11 is the precipitated ADU slurry collected from the South Uranium Plant, and XRD analysis reveal the primary compound to be ammonium uranium oxide hydrate (ADU). Sample 12851-04 is the precipitated ADU slurry collected from the NUFCOR plant, and, unsurprisingly, XRD analysis reveals the compounds to be identical with the sample 12850-11. Sample 12851-07 is the dried ADU product, and although the crystal structure is somewhat modified from the ADU slurry samples, it is still an ADU. Sample 12851-01 is the final calcined product, and is primarily U_3O_8 with trace U_2O_5 present.

Table 2 X-ray Diffraction Results

Series	Description	Major Phases Identified by XRD
Pair 1	**Palangana Ore**	Quartz; dolomite, Na-feldspar
	Hobson UOC	Uranyl peroxide
Pair 2	**Denison "Dirt" Ore**	Quartz; Dolomite; Kaolinite; possible minor uranium oxide phase
	Denison UOC	U_3O_8; UO_2
NUFCOR 12850-14	**Comminuted Ore Powder**	Quartz; Pyrophyllite; Chlorite, Muscovite
NUFCOR 12850-11	**ADU Slurry – South Uranium Plant**	$(NH_4)_2U_4O_{13}\cdot 7H_2O$ Ammonium Uranium Oxide Hydrate, Uranium Ammine Oxide Hydrate; $UO_3\cdot 2H_2O$ Metaschoepite, syn
NUFCOR 12851-04	**ADU Slurry NUFCOR Plant**	$(NH_4)_2U_4O_{13}\cdot 7H_2O$ Ammonium Uranium Oxide Hydrate, Uranium Ammine Oxide Hydrate; $UO_3\cdot 2H_2O$ Metaschoepite, syn
NUFCOR 12851-07	**Dried ADU product**	$U_3(NH_3)O_9\cdot 5H_2O$ Uranium Ammine Oxide Hydrate; $(UO_2)_3(SO_4)_2(OH)_2\cdot 8H_2O$ Zippeite
NUFCOR 12851-01	**Calcined U_3O_8 product**	U_3O_8; U_2O_5

Uranium Assay and Isotopic composition:

Results of uranium assay and isotopic composition measurements are presented in Tables 3-6. The results are discussed separately below for each sample set.

Palangana U-ore/Hobson UOC

The Palangana Ore and Hobson UOC samples were analyzed for U isotopic composition and concentration and the results are given in Table 3 and 4.. The Palangana sample is a low grade U ore (~0.0011 gU/g sample). The uranium is of natural isotopic composition, ^{236}U was below the detection limit although ^{234}U is significantly enriched relative to secular equilibrium with ^{238}U. The Hobson UOC sample is a typical uranyl peroxide UOC with a U concentration of 0.772 gU/g sample. The uranium is of natural isotopic composition, ^{236}U was below the detection limit, and ^{234}U is significantly depleted relative to secular equilibrium. The ^{234}U/^{238}U ratios differ between these paired samples far outside of analytical uncertainty, and are remarkable because they fall on opposite extremes of U isotopic composition of UOCs previously analyzed by our group (Figure 2).

Denison "Dirt" U-ore/Denison UOC

The Denison "Dirt" Ore and Denison UOC samples were analyzed for U isotopic composition and concentration and the data is listed in Table 3 and 4. The Denison "Dirt" sample is a low grade U ore (~0.0046 gU/g sample). The uranium is of natural isotopic composition, ^{236}U was below the detection limit, and ^{234}U is in secular equilibrium with ^{238}U. The Denison UOC sample is a U_3O_8 UOC with a U concentration of 0.799 gU/g sample. The uranium is of natural isotopic composition, ^{236}U was below the detection limit, and ^{234}U is in secular equilibrium. Although the two samples have ^{234}U/^{238}U isotopic ratios that differ outside analytical uncertainty, they are well within the typical range for UOCs and ores previously analyzed by our group.

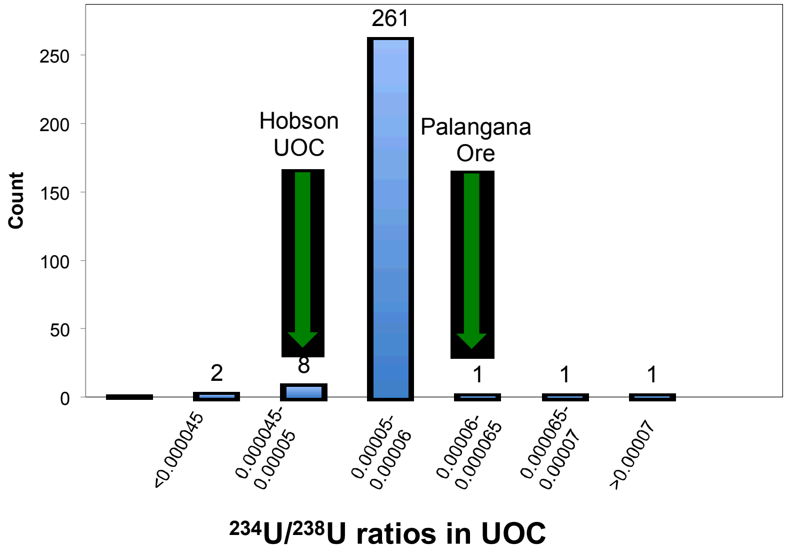

Figure 2 Histogram showing distribution of $^{234}U/^{238}U$ ratios in UOCs from known locations collected in the Uranium Sourcing Database. Approximately 4% of the UOCs have ^{234}U that is significantly depleted relative to secular equilibrium.

Table 3 Uranium Assay by ICP-MS and Davies Gray (D-G) titration (expanded uncertainties k=2).

Set	Sample	g U/g sample	Uncert.	Method
Pair 1	Palangana Ore	0.0011	0.004	ICP-MS
	Hobson UOC	0.772	0.0004	D-G
Pair 2	Denison "Dirt" Ore	0.0046	0.0011	ICP-MS
	Denison UOC	0.799	0.009	D-G

Table 4 Uranium isotopic ratios determined by MC-ICP-MS (expanded uncertainties k=2).

Set	Sample	U^{234} / U^{238}	Uncert.	U^{235} / U^{238}	Uncert.
Pair 1	Palangana Ore	0.000064127	0.00000010	0.0072516	0.0000038
	Hobson UOC	0.000047400	0.00000008	0.0072462	0.0000039
Pair 2	Denison "Dirt" Ore	0.000054432	0.000000087	0.0072523	0.0000038
	Denison UOC	0.000054857	0.000000089	0.0072504	0.0000039

Table 5 Uranium Assay by ICP-MS and Davies Gray titration (expanded uncertainties k=2).

Sample	Description	ug U/g sample	Uncertainty	Wt%	Uncert.	Method
12850-14	Comminuted Ore	331	8			ICP-MS
12850-01	Cleared Leachate Solution	112	10			ICP-MS
12850-03	Ion Exchange Eluate			0.311	0.006	D-G
12850-05	Loaded solution (OK liquor)			0.80	0.04	D-G
12850-11	ADU slurry (South Uranium Plant)			57.0 (as received)	0.3	D-G
12851-04	ADU Slurry (NUFCOR Plant)			58.4 (as received)	0.2	D-G
12851-07	Filtered and Dried ADU			69.4	0.3	D-G
12851-09	Calcined U_3O_8			78.6	0.4	D-G
12850-07	Stripped solution (raffinate)	259	12			ICP-MS
12850-09	ADU precipitate supernatant (Barren mother liquor)	0.99	0.08			ICP-MS

Table 6 Uranium isotopic ratios determined by MC-ICP-MS (expanded uncertainties k=2).

Sample	Description	U^{234} / U^{238}	Uncertainty	U^{235} / U^{238}	Uncert.
12850-14	Comminuted Ore	0.00005504	0.00000044	0.0072545	0.0000098
12850-01	Cleared Leachate Solution	0.00005323	0.00000036	0.0072543	0.0000075
12850-03	Ion Exchange Eluate	0.00005315	0.00000055	0.0072508	0.0000076
12850-05	Loaded solution (OK liquor)	0.00005313	0.00000054	0.0072553	0.0000075
12850-11	ADU slurry (South Uranium Plant)	0.00005327	0.00000017	0.0072502	0.0000077
12851-04	ADU Slurry (NUFCOR Plant)	0.00005318	0.00000018	0.0072499	0.0000078
12851-07	Filtered and Dried ADU	0.00005318	0.00000017	0.0072481	0.0000077
12851-09	Calcined U_3O_8	0.00005313	0.00000017	0.0072485	0.0000079
12850-07	Stripped solution (raffinate)	0.00005356	0.0000003	0.007252	0.0000078
12850-09	ADU precipitate supernatant (Barren mother liquor)	0.00005332	0.00000029	0.0072565	0.0000077

NUFCOR Samples-South Africa Samples

Uranium assay and isotopic analysis was performed on each of the NUFCOR samples, and the results are listed in Tables 5 and 6. The first sample in the series (12850-14) was a comminuted ore from which the gold had been removed. The U concentration of this sample is 331 ug/g. The cleared leach solution (12850-01) has a lower U concentration of 112 ug U/g. From this point in the processing stream, the uranium concentration in successive samples increases as the ore is refined to a composition of 78.6 wt% U in the final calcined U_3O_8 product. The ammonium sulfate raffinate sample (12850-07) has a U concentration of 259 ug U/g. Note that this solution is recycled back into the solvent extraction circuit and is therefore not expected to be devoid of U. The supernatant from the ADU slurry entering the NUFCOR plant was also sampled and has a U concentration of 0.99 ug U/g.

The uranium in all of the NUFCOR samples is of natural isotopic composition so that their $^{235}U/^{238}U$ isotopic compositions are indistinguishable within analytical uncertainty. The abundance of ^{236}U was below the detection limit for all samples. In contrast to the $^{235}U/^{238}U$ ratios, there are slight differences in the $^{234}U/^{238}U$ ratios across the sample suite. Specifically, the $^{234}U/^{238}U$ is slightly elevated in the comminuted ore (12850-14) compared to the other samples in the processing stream. Thus, there is a sharp decrease in the $^{234}U/^{238}U$ ratio in the first processing step from comminuted ore to leachate sample 12850-01 (Figure 3). The $^{234}U/^{238}U$ ratios are consistent within analytical uncertainty across the subsequent processing steps. Note that the $^{234}U/^{238}U$ ratio of the comminuted ore sample is slightly enriched relative to secular equilibrium, whereas the $^{234}U/^{238}U$ ratios of the other samples in the suite are slightly depleted relative to secular equilibrium.

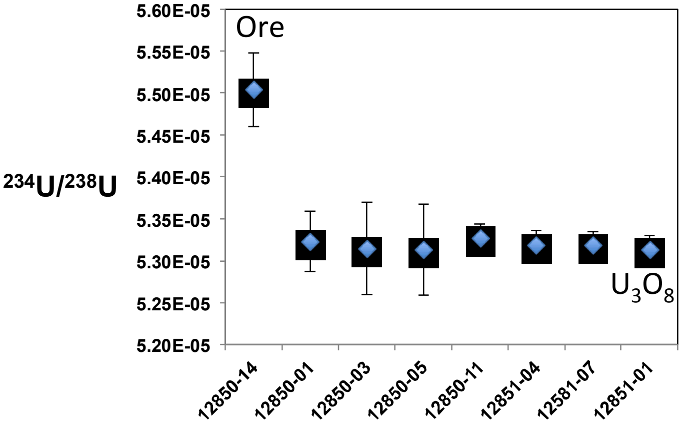

Figure 3 Changes of $^{234}U/^{238}U$ ratios across the NUFCOR sample suite. The $^{234}U/^{238}U$ ratio of the comminuted ore sample is significantly higher than the remainder of the sample suite.

U isotopes discussion:

There is great variability of the $^{234}U/^{238}U$ observed on earth (i.e. Kronfield, 1974; Sheng and Kuroda, 1984). This is typically attributed to degradation of mineral lattices by alpha recoil resulting in the greater mobility of alpha decay products during subsequent weathering and alteration (i.e. Fleischer, 1988). Water that has permeated a U-bearing formation typically becomes enriched in ^{234}U relative to ^{238}U, whereas the rock typically becomes depleted in ^{234}U.

The Palangana and NUFCOR comminuted ores appear to have more complex ^{234}U isotopic systematics, however. Both the Palangana and NUFCOR comminuted ores are enriched in ^{234}U relative to ^{238}U. This likely reflects the fact that these ore bodies represent deposition U mobilized from source rocks during weathering and alteration. In this scenario, groundwater first infiltrates a U bearing formation preferentially leached ^{234}U relative to other U isotopes. This U is then deposited in the sedimentary rocks of the Goliad Formation resulting in a ^{234}U enriched ore (e.g. Uvarova et al., 2014). This effect is quite pronounced in the Palangana ore, but more subtle in the NUFCOR ore. Note that in this scenario, U deposition must have occurred relatively recently, otherwise secular equilibrium would be re-established as ^{234}U decays. Interestingly, the Denison "Dirt" ore sample is in secular equilibrium, implying that the uranium was not recently mobilized during interaction with a water.

Although ^{234}U is more readily mobilized than the other isotopes of U, the UOC from Hobson (produced from the sampled Palangana ore) is depleted in ^{234}U. This likely reflects the ISR mining technique employed at the Palangana mine. In situ recovery (ISR) mines cycle large volumes of lixiviant through the sedimentary formation. Because ^{234}U is more easily mobilized, this isotope is likely removed from the rock formations in preference to the other U isotopes. In this case, UOC produced early in the development of an ISR field would likely have a relatively high ^{234}U/^{238}U ratio which would progressively decrease as the formation becomes depleted in U with time. In fact, ^{234}U/^{238}U ratios from samples from drill holes fully exploited ISR mine units at the SmithRanch/Highlands Mine in Wyoming typically have significantly depleted ^{234}U/^{238}U ratios (WoldeGabriel et al., 2014). Thus, the large difference in ^{234}U/^{234}U ratios from the ore to UOC may reflect a UOC produced late in the production life of the mine unit from which the ore was sampled.

The NUFCOR series also shows a decrease in ^{234}U relative to ^{238}U between the comminuted ore and the subsequent samples. The decrease is far less pronounced than in the Palangana/Hobson pair. One possibility is that the enriched ^{234}U is hosted in secondary phases (i.e. clays) that are less easily leached than the primary U ore phases. In this case, the leachate produced from the comminuted ore reflects the isotopic composition of more easily leached primary U phases, and the more difficult to leach clays are less reflected in the leachate. It is interesting to note that subsequent processing steps do not appear to affect the U isotopic composition of the product. As a consequence, the ^{234}U/^{238}U ratio remains constant after leaching.

Major, Minor, and Trace Elements:

Major, minor, and trace elements were measured by quadrupole ICP-MS and XRF. Results of these analyses are presented in Tables 7-14.

Each sample was analyzed for trace elements in triplicate so that three aliquots of each sample were crushed, digested, and analyzed for trace elements separately. Thus, each aliquot represents an independent measurement of the sample. Table 7 lists the average values for the three separate analytical runs on the Palangana Ore, Hobson UOC, the Denison "Dirt" ore, and Denison UOC. Table 8 lists the average values for the preliminary products of U processing stream collected at the South Uranium Plant, South Africa. These preliminary products include the comminuted ore, cleared leach solution, ion exchange eluate, and the loaded solution (OK liquor). Table 9 lists the average values for the final post precipitation products including ADU collected from the South Uranium and NUFCOR Plants.

Figure 4 demonstrates the efficiency with which various trace elements are removed from the parent ores during processing of Palangana/Hobson and Denison mine products. Most of the elements in the ores are significantly reduced in concentration in the associated UOCs (Figure 4). Several exceptions stand out. In the Hobson UOC, the concentrations of Cl, Se, and Sn are higher than in the original Palangana ore. This implies that although the processing circuits efficiently remove most of the trace impurities, Cl, Se and Sn are concentrated in the UOC. Chlorine is not detectable in the ore, but is 900 ug/g in the final UOC product. This is not surprising because NaCl is used in the processing of the ore and likely represents a contaminant in the final product. Selenium is also likely associated with the reagents used in processing the ore. A striking feature of Figure 4 is the progressive depletion of the rare earth elements from heaviest to lightest demonstrating the preferential removal of light rare earth elements over heavy rare earth elements during processing.

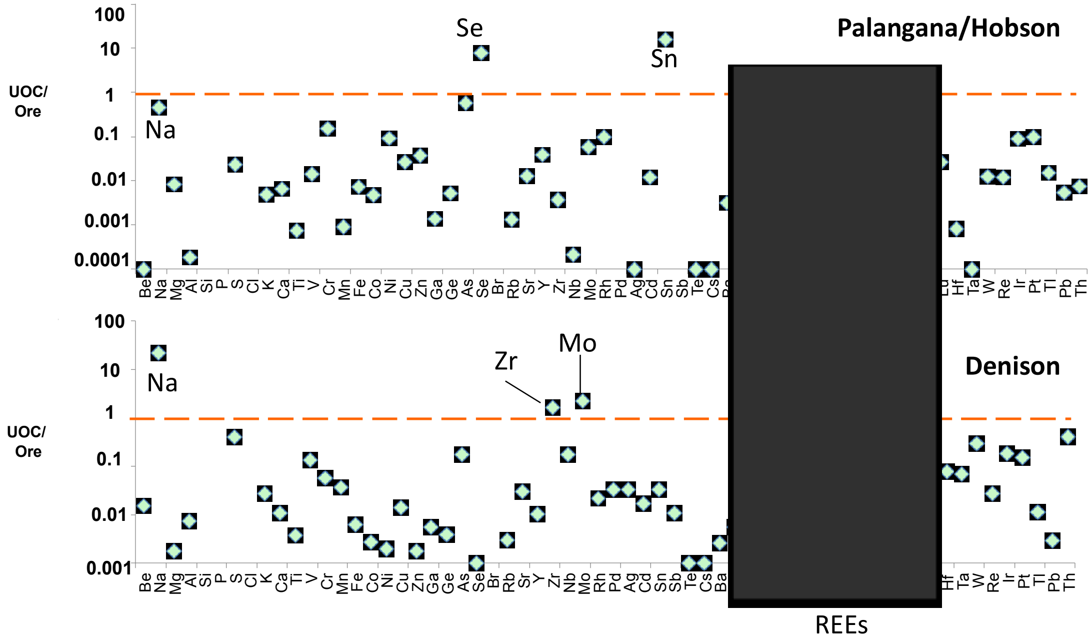

Figure 4. Plot showing trace element concentrations in UOC normalized to concentrations in associated U ore for sample from Palangana/Hobson and Denison. Values greater than 1 indicate that the element is concentrated during processing, whereas values less than 1 indicate the element is

removed during processing. Greater negative deviations from unity indicate more efficient removal of the impurity. The rare earth elements form a linear array from lightest to heaviest in both ore/UOC pairs, indicating that the light rare earths are more efficiently removed than the heavy rare earth elements. This effect is more pronounced in the Palangana/Hobson pair than in the Denison pair. A) Most elements are efficiently removed from the Palangana Ore, although Se and Sn are actually concentrated in the ore. It is notable that Na and As are near unity, indicating very inefficient removal or secondary addition of these elements during processing. B) Na, Zr and Mo are concentrated in the Denison ore relative to the Denison UOC.

Sodium, zirconium, and molybdenum occur in greater concentrations in the Denison UOC than in the corresponding ore (Figure 4B). Molybdenum follows U during processing and is therefore likely to be concentrated from the ore into the final UOC product. Elevated Na in the UOC may reflect the fact that is was added during processing. It is unclear where the Zr is derived from, but may be added as a component of one of the reagents used to process the ore.

Figures 5 and 6 illustrate the efficiency with which various trace elements are removed from the parent ores during processing of South African NUFCOR. The concentrations of nearly all elements are reduced in processed samples relative to the parent ores. The notable exception is Cl, which is added during processing. It is apparent that concentrations of impurities progressively decrease in the leaching, ion exchange, and solvent extraction steps. The concentrations of trace elements are fairly constant from the ADU slurry to the dried ADU. The final calcined U_3O_8 has fewer elemental impurities than the ADU, although the reductions in concentration are not as dramatic as in the first steps in the milling process.

Rare earth element concentrations are presented in Tables 11-14 and plotted on chondrite normalized diagrams in Figures 7 and 8. Although the REE pattern of the original ore from the Denison “Dirt” ore sample is partially preserved in the Denison UOC, the REE pattern from the Palangana ore is not preserved in the UOC from the Hobson plant. The REE patterns of the South African suite are not modified significantly throughout the processing stages, although the shapes of the patterns change slightly. It is clear that in all samples the ratio light rare earth elements to heavy rare earth elements are fractionated to various degrees from the original ore. We speculate that this may reflect incomplete elution of REEs from the ion exchange columns. In any case, the fractionation of REE during processing observed here casts doubt on the common interpretation that REE patterns in UOC are representative of the parent ore.

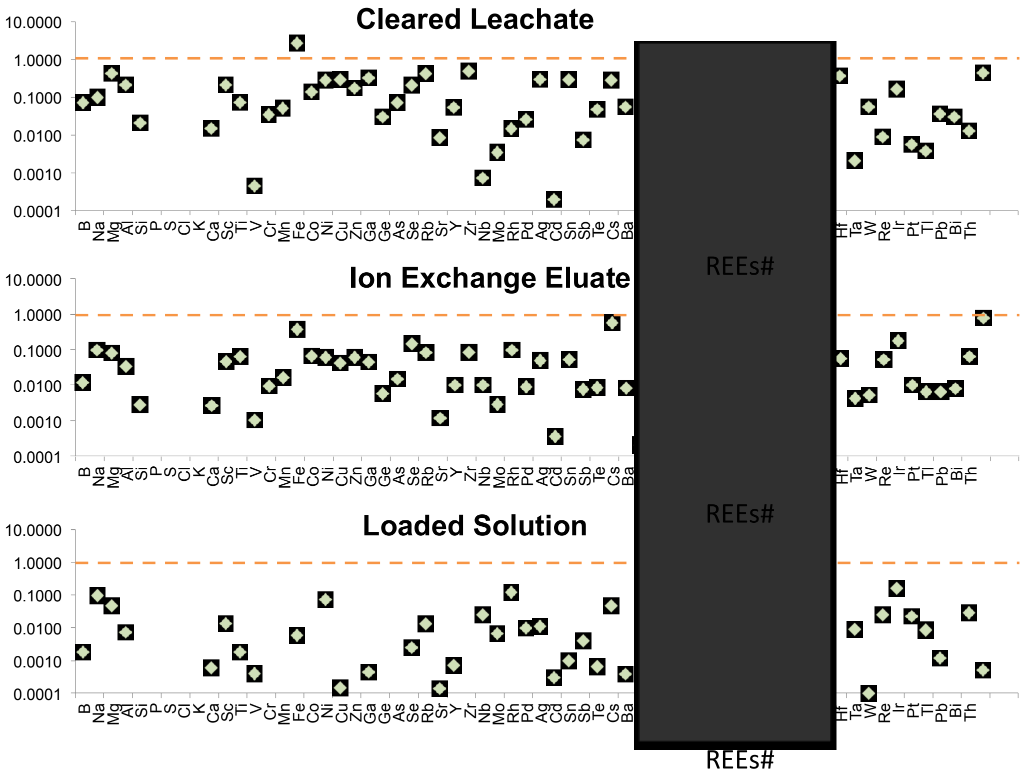

Figure 5. Plot showing trace element concentrations in UOC normalized to concentrations in associated U ore for samples from South African NUFCOR. A) the cleared leachate solution shows fractionated recovery of rare earth elements from the ore, and decreases in every element except Fe; B) the ion exchange eluate shows significant reductions in impurities over the cleared leachate solution, the reduction in concentrations for transition metals and rare earth elements is approximately an order of magnitude less than the cleared leachate solution; C) the loaded solution has the lowest concentration of all elements, and all rare earth element concentrations are below detection limits.

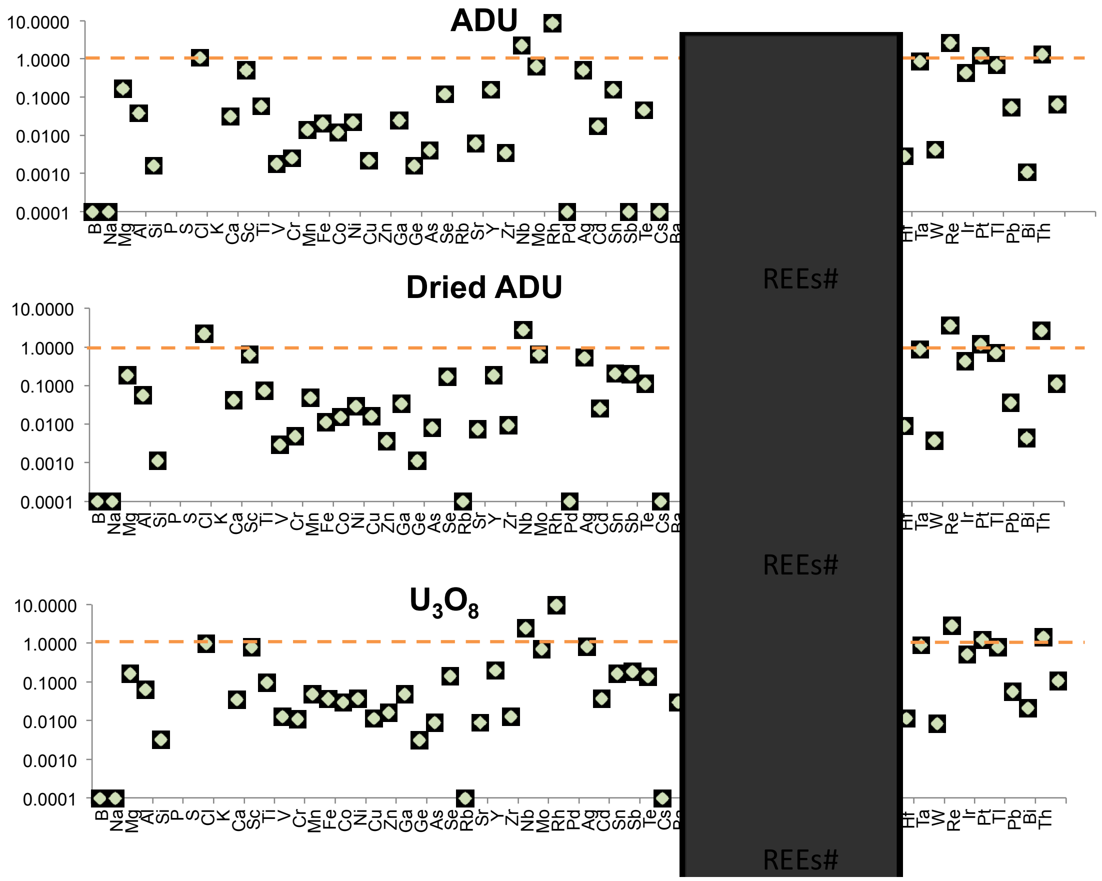

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Figure 6. Plot showing trace element concentrations in UOC normalized to concentrations in associated U ore for samples from South African NUFCOR. A) Most elemental abundances are similar to the loaded solution in the ADU slurry although Cl is actually in greater abundance than in the previous products. The two ADU samples from South Uranium Plant and the NUFCOR plant are essentially identical. B) The dried ADU product has a similar trace element pattern to the ADU. Note the presence of excess Cl in the dried ADU product. C) The U_3O_8 calcined final product has lower abundances of impurities than previous samples in the suite, and the rare earth elements appear somewhat less depleted in the lightest elements than in previous steps.

Table 7 Major, Minor, and Trace Elements for Palangana/Hobson and Denison Ore/UOC pairs.

	Palangana Ore ug/g	95% CL.	Hobson UOC ug/g	95% CL.	Denison "Dirt" Ore ug/g	95% CL.	Denison UOC ug/g	95% CL.
Be	1.28	0.19	-0.02	0.04	1.31	0.18	0.02	0.06
Na	12300	900	5600	500	314	10	6800	600
Mg	1800	400	15.1	1.9	7000	1100	12.8	1.8
Al	27000	7000	5	12	21000	3000	160	20
Si	239000	3000	< 254		228000	2000	< 250	
P	4800	350	< 227		780	350	< 195	
S	33300	660	790	142	9430	350	3800	275
Cl	< 59	---	900	207	1100	170	< 110	
K	18700	1500	90	30	9500	400	260	50
Ca	43000	3000	290	70	23000	6000	250	50
Ti	2000	300	1.5	0.8	1260	70	4.8	0.7
V	35	11	0.5	0.2	190	50	25.6	1.2
Cr	13	3	2	4	43	5	2.5	0.2
Mn	240	40	0.22	0.11	110	70	4.1	0.6
Fe	11000	2000	80	40	50000	40000	320	50
Co	3.2	0.4	0.015	0.009	300	200	0.83	0.1
Ni	5.4	0.4	0.5	0.4	500	200	1	0.3
Cu	7.4	1	0.2	0.5	4100	400	58	2
Zn	32	7	1.2	1.5	2800	400	5	5
Ga	9.5	1	0.013	0.019	4.7	0.3	0.026	0.019
Ge	1.9	0.16	0.01	0.06	5	0.9	0.02	0.06
As	5.1	1	3	2	1300	800	233	8
Se	1	1.9	8	7	110	30	-1	6
Br	< 14	---	< 76		< 12	---	< 73	
Rb	53	7	0.07	0.07	26.4	1.3	0.08	0.07
Sr	304	10	3.9	0.6	530	150	16.3	1
Y	7.5	1.6	0.3	0.04	23	5	0.24	0.03
Zr	106	10	0.39	0.12	97	7	155	8
Nb	14	3	0.003	0.006	3.75	0.16	0.66	0.11
Mo	190	70	11	2	250	20	549	19
Ru	0.001	0.006	0.002	0.006	0.003	0.007	0.006	0.013
Rh	0.006	0.003	0.0006	0.0012	0.036	0.012	0.0008	0.0016
Pd	0.16	0.05	0	0.03	0.3	0.1	0.01	0.02
Ag	0.24	0.04	-0.02	0.07	9	10	0.3	0.11
Cd	0.41	0.1	0.005	0.019	7	3	0.12	0.12
Sn	1.2	0.7	19.1	1.1	0.6	0.3	0.02	0.08
Sb	0.8	0.7	0	0.07	5.5	0.3	0.06	0.12
Te	0.03	0.07	-0.2	0.6	0.01	0.04	-0.1	0.4
Cs	1.7	0.3	-0.02	0.1	1.6	0.12	-0.02	0.11
Ba	440	90	1.4	0.3	1300	900	3.4	0.3
Hf	2.45	0.18	0.002	0.002	2.4	0.2	0.19	0.03
Ta	0.79	0.07	-0.0012	0.0019	0.54	0.15	0.037	0.005
W	0.8	0.4	0.01	0.03	3.6	0.5	1.08	0.12
Re	3	3	0.036	0.01	0.36	0.06	0.01	0.006

Ir	0.011	0.003	0.001	0.0016	0.011	0.003	0.002	0.002
Pt	0.03	0.007	0.003	0.004	0.026	0.012	0.004	0.006
Tl	0.32	0.03	0.005	0.005	20	16	0.23	0.05
Pb	9.3	1.2	0.05	0.11	800	700	2.3	0.5
Th	2.9	0.4	0.022	0.006	2.15	0.18	0.88	0.06

Table 8 Major, Minor, and Trace Elements for Samples from the preliminary stages of U extraction.

	12850-14 Comminuted Ore	95% CL.	12850-01 Cleared leachate solution	95% CL.	12850-03 IX eluate	95% CL.	12850-05 loaded solution (OK liquor)	95% CL.
	ug/g		ug/g		ug/g		ug/g	
Be	1.1	0.7	0.08	0.03	0.013	0.012	0.002	0.005
B	2	5	0.2	0.2	0.2	0.2	0.2	0.2
Na	1060	60	460	90	87	18	51	10
Mg	1720	150	370	60	60	12	13	2
Al	35000	5000	750	150	100	20	0.49	0.11
Si	370000	2845	n.m.	n.m.	n.m.	n.m.	n.m.	n.m.
P	null	null	n.m.	n.m.	n.m.	n.m.	n.m.	n.m.
S	5040	258	n.m.	n.m.	n.m.	n.m.	n.m.	n.m.
Cl	null	null	n.m.	n.m.	n.m.	n.m.	n.m.	n.m.
K	9800	900	150	30	26	7	6	2
Ca	1100	130	240	40	51	10	15.6	1.6
Sc	4.8	0.9	0.36	0.05	0.32	0.05	0.009	0.003
Ti	700	400	0.32	0.09	0.74	0.12	0.28	0.14
V	28	3	0.98	0.14	0.27	0.04	0.0001	0.0005
Cr	160	100	8.1	1.2	2.7	0.4	0.01	0.03
Mn	186	8	520	60	71	10	1.12	0.1
Fe	12300	800	1700	300	850	110	0.3	0.3
Co	38	5	10.8	1.5	2.3	0.3	2.8	0.3
Ni	100	40	30	4	4.4	0.7	0.015	0.019
Cu	38	3	6.7	0.8	2.3	0.3	0.0036	0.002
Zn	130	30	42	4	5.9	0.6	0.06	0.02
Ga	12	2	0.37	0.07	0.071	0.014	0.0003	0.0006
Ge	5.3	1.1	0.39	0.1	0.08	0.03	0.0002	0.0015
As	166	18	35	3	25	3	0.41	0.02
Se	6	5	2.5	0.8	0.5	0.2	0.08	0.11
Br	null	null	n.m	n.m	n.m	n.m	n.m	n.m
Rb	47	5	0.4	0.03	0.058	0.007	0.0065	0.0017
Sr	37	3	2.05	0.13	0.38	0.02	0.027	0.003
Y	12.5	1.8	6.3	0.3	1.07	0.05	0.0004	0.0002
Zr	111	16	0.084	0.008	1.12	0.07	2.77	0.08
Nb	4.4	1.8	0.0155	0.0012	0.013	0.001	0.0299	0.0015
Mo	2.3	1.3	0.034	0.005	0.231	0.011	0.287	0.014
Ru	-0.0001	0.0016	0.00003	0.00007	0.00014	0.0002	0.00008	0.00011
Rh	0.011	0.004	0.00029	0.0001	0.0001	0.00005	0.00011	0.00004
Pd	0.018	0.008	0.0055	0.0008	0.0009	0.0004	0.0002	0.00015
Ag	0.8	0.2	0.00016	0.00017	0.0003	0.0005	0.00024	0.0002
Cd	0.41	0.1	0.122	0.007	0.022	0.002	0.0004	0.0004
Sn	0.91	0.17	0.0069	0.0017	0.0071	0.0011	0.0036	0.0013
Sb	1.8	0.2	0.086	0.004	0.016	0.0018	0.0012	0.0008
Te	0.19	0.14	0.054	0.015	0.11	0.02	0.009	0.006
Cs	2.6	0.3	0.146	0.004	0.022	0.002	0.001	0.0015

Ba	215	14	0.002	0.002	0.045	0.004	0.008	0.002
Hf	3.2	0.5	0.0068	0.0009	0.014	0.003	0.029	0.006
Ta	1.1	0.3	0.062	0.005	0.006	0.0012	0	0.00011
W	0.47	0.06	0.0043	0.0007	0.025	0.004	0.012	0.003
Re	0.003	0.003	0.0005	0.00013	0.00055	0.00011	0.00048	0.00014
Ir	0.007	0.002	0.00004	0.00005	0.00007	0.00003	0.00016	0.00007
Pt	0.023	0.006	0.00009	0.00006	0.00015	0.00012	0.0002	0.00011
Tl	0.4	0.04	0.015	0.002	0.0026	0.0006	0.0005	0.0003
Pb	138	14	4.2	0.2	1.13	0.15	0.0005	0.0006
Bi	0.87	0.09	0.0112	0.0015	0.058	0.009	0.025	0.006
Th	38	7	17	2	30	6	0.02	0.006

n.m. = not measured

Table 9 Major, Minor, and Trace Elements for Samples from final stages of U extraction.

	12850-11 ADU Slurry ug/g U	95% CL.	12851-04 ADU Slurry ug/g U	95% CL.	12581-07 Filtered ADU ug/g U	95% CL.	12851-01 Calcined U3O8 ug/g U	95% CL.
Be	-0.12	0.08	-0.12	0.09	-0.12	0.09	-0.11	0.06
B	-2	4	-1	5	-2	4	-2	4
Na	250	80	250	80	280	100	230	80
Mg	90	20	100	30	140	40	140	40
Al	79	3	91	3	58	7	151	20
Si	n.m.	n.m.	n.m.	n.m.	n.m.	n.m.	n.m.	n.m.
P	n.m.	n.m.	n.m.	n.m.	n.m.	n.m.	n.m.	n.m.
S	7800	400	5400	300	15900	500	6500	300
Cl	n.m.	n.m.	n.m.	n.m.	n.m.	n.m.	n.m.	n.m.
K	440	80	410	100	590	100	430	90
Ca	800	200	900	200	1000	200	1100	300
Sc	0.4	1.3	0.4	1.4	0.5	1.5	0.6	1.3
Ti	1.8	0.8	2.3	1.7	3	2	12	9
V	0.1	0.3	0.21	0.13	0.2	0.4	0.4	0.3
Cr	3.1	1.4	5	8	11	4	10	5
Mn	5.4	1	4.8	1.4	3	0.8	9	4
Fe	210	30	160	50	270	50	480	60
Co	1.21	0.11	1.41	0.07	1.64	0.12	1.87	0.06
Ni	0.3	0.6	1	3	2.28	0.19	1.5	1.4
Cu	-0.1	0.3	0.1	0.8	0.2	0.6	0.8	0.4
Zn	4.6	0.6	4.5	0.7	6.3	0.3	8.3	0.8
Ga	0.027	0.016	0.029	0.012	0.02	0.014	0.05	0.015
Ge	0.03	0.03	0.04	0.02	0.06	0.04	0.06	0.02
As	29.1	1.4	28.2	1.3	40.3	1.1	29.8	0.8
Se	0	3	-0.2	1.9	0.2	2	-0.2	1.8
Br	n.m.	n.m.	n.m.	n.m.	n.m.	n.m.	n.m.	n.m.
Rb	0.41	0.17	0.39	0.15	0.5	0.2	0.55	0.14
Sr	8.2	0.2	8.2	0.3	9.9	0.5	9.4	0.4
Y	0.062	0.005	0.061	0.01	0.172	0.01	0.205	0.009
Zr	356	19	358	16	450	30	350	19
Nb	3.98	0.1	3.96	0.1	3.96	0.14	3.97	0.11
Mo	28	4	28	4	51	8	29	4
Ru	0.002	0.004	0.002	0.004	0.002	0.002	0.002	0.005
Rh	-0.0003	0.0009	-0.0002	0.0008	-0.0002	0.0009	0	0.0009
Pd	0.013	0.011	0.015	0.011	0.014	0.01	0.019	0.017
Ag	0.02	0.11	0.03	0.14	0.03	0.14	0.04	0.13
Cd	0.09	0.05	0.09	0.05	0.12	0.09	0.09	0.06
Sn	-0.02	0.02	0.008	0.014	0.26	0.03	0.22	0.15
Sb	0.116	0.014	0.13	0.017	0.29	0.03	0.32	0.04
Te	-0.13	0.15	-0.12	0.14	-0.11	0.15	-0.11	0.13
Cs	0	0.3	0.1	0.3	0	0.2	0.1	0.3
Ba	4.6	0.3	3.9	0.3	4.23	0.15	6.9	1.1
Hf	3.88	0.09	3.88	0.11	3.99	0.13	3.79	0.1

Ta	0.0066	0.0014	0.009	0.009	0.006	0.003	0.012	0.003
W	1.77	0.07	1.77	0.07	2.39	0.09	1.76	0.08
Re	0.0018	0.0019	0.0018	0.0016	0.0018	0.002	0.002	0.0012
Ir	0.012	0.004	0.013	0.004	0.012	0.003	0.011	0.003
Pt	0.023	0.008	0.025	0.013	0.023	0.007	0.023	0.007
Tl	0.03	0.02	0.03	0.02	0.02	0.03	0.03	0.03
Pb	0.21	0.04	0.24	0.06	0.89	0.16	3.8	0.2
Bi	1.59	0.07	1.66	0.07	3.38	0.19	1.65	0.08
Th	3.5	0.6	3.2	0.5	6.1	1	5.2	0.9

Table 10 Major, Minor, and Trace Elements for Samples from barren solutions, NUFCOR, South Africa.

	12850-07 Stripped solution (raffinate) ug/g	95% CL.	12850-09 barren mother liquor ug/g	95% CL.
Be	0.011	0.013	0.002	0.007
B	0.2	0.3	0.05	0.16
Na	610	150	50	8
Mg	51	11	12	2
Al	84	20	0.4	0.11
Si	n.m.	n.m.	n.m.	n.m.
P	n.m.	n.m.	n.m.	n.m.
S	n.m.	n.m.	n.m.	n.m.
Cl	n.m.	n.m.	n.m.	n.m.
K	23	6	5.3	1.7
Ca	47	9	14	4
Sc	0.24	0.03	0.0002	0.0008
Ti	0.59	0.11	0.24	0.06
V	0.22	0.04	0	0.0005
Cr	2.1	0.4	-0.003	0.004
Mn	56	8	1.17	0.11
Fe	660	90	-0.02	0.07
Co	1.9	0.3	2.7	0.3
Ni	3.5	0.5	0.014	0.015
Cu	1.8	0.3	0.01	0.02
Zn	4.3	0.5	0.046	0.011
Ga	0.056	0.013	0.0001	0.0003
Ge	0.06	0.02	-0.0001	0.0009
As	19	2	0.117	0.015
Se	0.4	0.2	0.03	0.19
Br	n.m.	n.m.	n.m.	n.m.
Rb	0.049	0.008	0.0053	0.0014
Sr	0.343	0.02	0.0068	0.0016
Y	0.85	0.06	0.00018	0.00019
Zr	0.34	0.02	0.027	0.002
Nb	0.0073	0.0015	0.00029	0.00013
Mo	0.126	0.008	0.013	0.002
Ru	0.00011	0.00017	0.00004	0.00011
Rh	0.00007	0.00004	0.00011	0.00005
Pd	0.0008	0.0003	0.0004	0.0003
Ag	0.0005	0.0004	0.00022	0.00019
Cd	0.017	0.0019	0.0002	0.00019
Sn	0.0054	0.0008	0.00024	0.00018
Sb	0.0157	0.0017	0.0004	0.0002
Te	0.08	0.03	-0.0001	0.0003

Cs	0.0181	0.0016	0.00028	0.00018
Ba	0.056	0.005	0.0008	0.001
Hf	0.0056	0.0005	0.00035	0.00019
Ta	0.0059	0.0003	-0.00003	0.00011
W	0.018	0.003	0.0005	0.001
Re	0.001	0.0003	0.00051	0.00015
Ir	0.00004	0.00004	0.00016	0.00008
Pt	0.00015	0.00008	0.00008	0.00005
Tl	0.0022	0.0004	0.0006	0.0004
Pb	0.91	0.1	0.0003	0.0005
Bi	0.041	0.007	0.0103	0.0018
Th	24	4	0.00027	0.00008

Table 11 Rare earth element concentrations for Palangana/Hobson and Denison UOC/Ore pairs.

	Palangana Ore μg/g sample	95% CI	Hobson UOC μg/g sample	95% CI	Denison “Dirt” Ore μg/g sample	95% CI	Denison UOC μg/g sample	95% CI
La	15	2	0.013	0.007	11.6	1.3	0.064	0.016
Ce	29	3	0.042	0.009	27.6	1.8	0.147	0.014
Pr	3.2	0.5	0.0036	0.0013	4.2	0.5	0.023	0.005
Nd	11.5	1.9	0.019	0.009	17.6	1.4	0.1	0.02
Sm	2.1	0.3	0.006	0.007	3.9	0.4	0.03	0.008
Eu	0.32	0.07	0.0021	0.0019	0.4	0.4	0.006	0.003
Gd	1.8	0.3	0.008	0.004	4.6	0.7	0.033	0.011
Tb	0.086	0.013	0.0018	0.0011	0.46	0.07	0.0058	0.0013
Dy	1.4	0.3	0.013	0.005	3.7	0.5	0.034	0.008
Ho	0.26	0.04	0.0044	0.0015	0.67	0.11	0.0074	0.0016
Er	0.8	0.11	0.017	0.006	1.9	0.3	0.022	0.006
Tm	0.12	0.03	0.0024	0.0007	0.24	0.04	0.004	0.002
Yb	0.86	0.16	0.019	0.005	1.6	0.2	0.026	0.008
Lu	0.12	0.02	0.0033	0.0013	0.2	0.04	0.0038	0.0011

Table 12 Rare earth element concentrations for samples from the preliminary stages of U extraction, NUFCOR/South Africa .

	12850-14 Comminuted Ore		**12850-01 cleared leachate solution**		**12850-03 IX eluate**		**12850-05 loaded solution (OK liquor)**	
	µg/g sample	**95% CI**	**µg/g sample**	**95% CI**	**µg/g sample**	**95% CI**	**µg/g sample**	**95% CI**
La	34	3	1.54	0.03	0.269	0.014	0.00024	0.00007
Ce	65	6	3.95	0.08	0.71	0.04	0.00012	0.00011
Pr	7.8	1.2	0.52	0.012	0.093	0.006	0.000026	0.00002
Nd	24	3	2.23	0.08	0.4	0.03	0.00013	0.00011
Sm	4.8	0.5	0.95	0.04	0.18	0.013	0.00005	0.00005
Eu	0.8	0.11	0.158	0.008	0.03	0.003	0.000011	0.000011
Gd	3.7	0.4	1.4	0.06	0.26	0.02	0.00007	0.00006
Tb	0.6	0.09	0.277	0.011	0.051	0.005	0.00001	0.000007
Dy	3.2	0.4	1.74	0.1	0.31	0.03	0.00005	0.00003
Ho	0.66	0.11	0.322	0.017	0.056	0.006	0.000011	0.00001
Er	1.8	0.3	0.87	0.05	0.147	0.016	0.000023	0.00002
Tm	0.26	0.05	0.12	0.006	0.0197	0.0019	0.000004	0.000003
Yb	1.6	0.2	0.7	0.05	0.113	0.014	0.00003	0.00003
Lu	0.22	0.04	0.082	0.007	0.0128	0.0017	0.000003	0.000004

Table 13 Rare earth element concentrations for samples from the final stages of U extraction, NUFCOR/South Africa .

	12850-11 ADU Slurry	Uncert.	12851-04 ADU Slurry	Uncert.	12581-07 Filtered ADU	Uncert.	12851-01 Calcined U3O8	Uncert.
	ug/g U		ug/g U		ug/g U		ug/g U	
La	0.071	0.019	0.078	0.016	0.056	0.018	0.26	0.19
Ce	0.199	0.009	0.215	0.009	0.18	0.006	0.6	0.3
Pr	0.0225	0.0018	0.0231	0.0015	0.0221	0.0018	0.07	0.04
Nd	0.083	0.007	0.087	0.005	0.094	0.008	0.27	0.13
Sm	0.019	0.006	0.02	0.005	0.038	0.006	0.059	0.014
Eu	0.0037	0.0007	0.0034	0.0008	0.0067	0.0016	0.007	0.0017
Gd	0.019	0.004	0.017	0.003	0.047	0.007	0.054	0.008
Tb	0.0026	0.0007	0.0026	0.0008	0.0096	0.0014	0.0084	0.0018
Dy	0.015	0.002	0.016	0.003	0.059	0.006	0.051	0.004
Ho	0.0031	0.0007	0.003	0.0008	0.0106	0.0014	0.0096	0.0017
Er	0.011	0.003	0.01	0.002	0.031	0.005	0.029	0.004
Tm	0.0012	0.0004	0.0012	0.0004	0.0041	0.0007	0.004	0.0006
Yb	0.0069	0.0017	0.007	0.003	0.025	0.004	0.025	0.004
Lu	0.0009	0.0003	0.001	0.0004	0.0029	0.0006	0.0033	0.0006

Table 14 Rare earth element concentrations for samples from the barren liquids, NUFCOR, South Africa .

	12850-07 Stripped solution (raffinate) ug/g	uncertainty	12850-09 barren mother liquor ug/g	uncertainty
La	0.218	0.005	0.00002	0.00003
Ce	0.577	0.018	0.00002	0.00014
Pr	0.076	0.003	0.000011	0.000011
Nd	0.326	0.019	0.00004	0.00006
Sm	0.148	0.01	0.00001	0.00003
Eu	0.0247	0.0019	0.000006	0.000009
Gd	0.211	0.014	0.00004	0.00004
Tb	0.042	0.003	0.000004	0.000005
Dy	0.26	0.02	0.00002	0.00003
Ho	0.046	0.004	0.000004	0.000004
Er	0.12	0.011	0.000009	0.000012
Tm	0.0162	0.0011	0.000001	0.000002
Yb	0.093	0.011	0.000001	0.000011
Lu	0.0105	0.0013	0.000001	0.000002

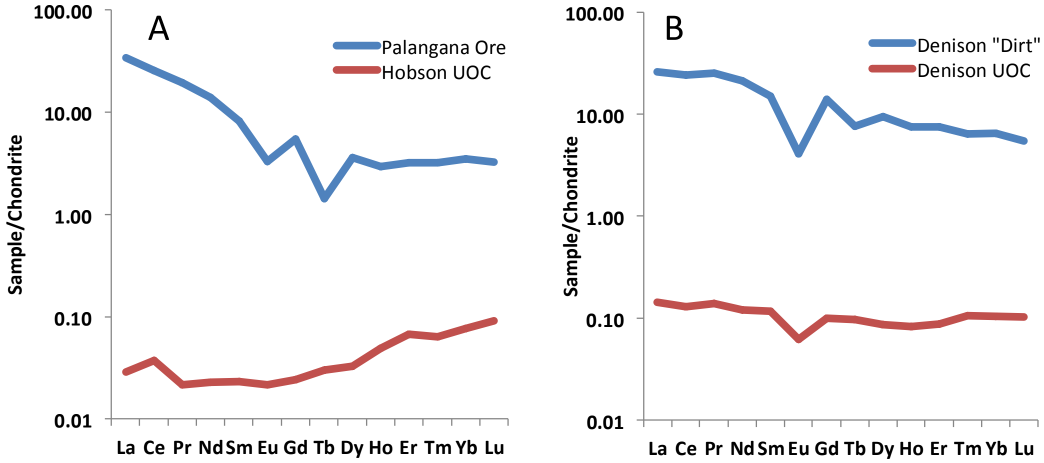

Figure 7 Chondrite normalized REE patterns of the Palangana/Hobson and Denison paired ore and UOC samples. A) The REE pattern of the Hobson UOC is significantly depleted in light REEs relative to the Palangana ore sample. Also, the Eu anomaly present in the ore REE pattern is not transmitted to the UOC. B) The Denison "Dirt" ore and Denison UOC have similar REE patterns, and in this case the Eu anomaly is preserved in the UOC signature. The light REEs, while somewhat depleted in the UOC relative to the ore (i.e. Figure 4) are far less fractionated in this UOC.

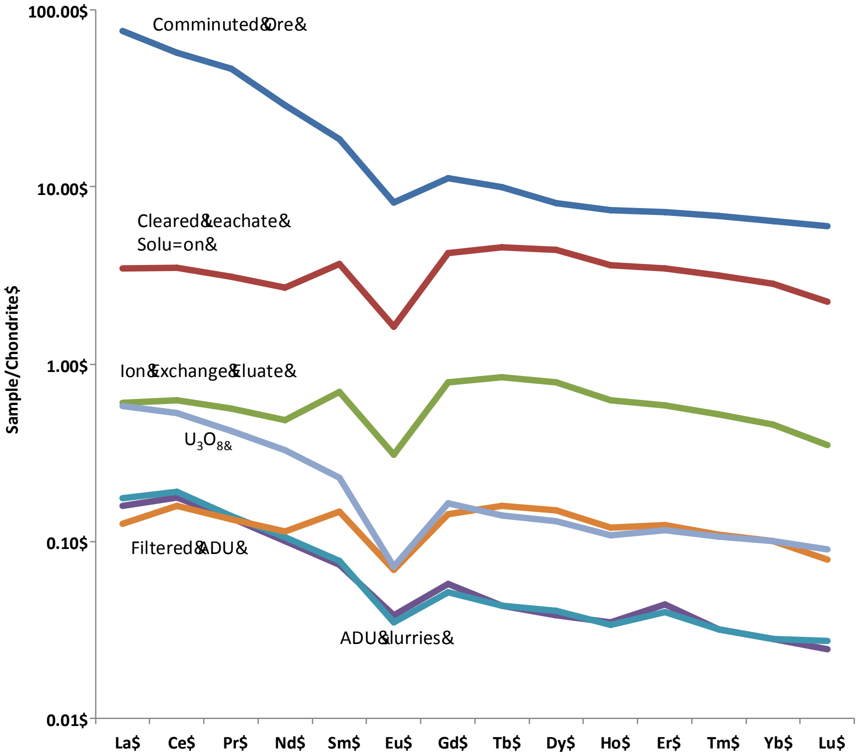

Figure 8 Chondrite normalized rare earth element patterns for the South African NUFCOR Ore and UOC products and intermediates. The absolute REE concentrations decrease through the processing steps, although the Eu anomaly is preserved. It is also interesting to note that the leachate solution, and ion exchange eluate samples have relatively flat light REE patterns, in contrast to the ore, ADU, and U_3O_8 samples.

Pb Isotopes:

Lead isotopic ratios are tabulated in Tables 15 and 16. Lead isotopes are of interest in tracing the modification of isotopic signatures through processing because ^{206}Pb is the decay product of ^{238}U, ^{207}Pb is the decay product of ^{235}U, and ^{208}Pb is the decay product of ^{232}Th. In contrast, ^{204}Pb is not radiogenic, and is therefore useful for estimating the fraction of the other lead isotopes in a given sample that are not produced in situ by decay of U and Th in the ore body. In other words, ^{204}Pb can be used to evaluate how much Pb has been produced by decay in the ore body since it formed (Stacey and Kramers, 1975). Ancient U ores with high U/Pb ratios are commonly enriched in ^{207}Pb and ^{206}Pb, whereas ancient Th ores usually have elevated ^{208}Pb.

The ^{206}Pb/^{204}Pb and ^{207}Pb/^{204}Pb compositions of the Palangana Ore sample are essentially indistinguishable from average crustal lead (i.e. common Pb, Stacey and Kramers, 1975), indicating that the ore body is either young or not significantly enriched in U relative to Pb (Figure 9). This is consistent with the very low concentration of U in the Goliad formation from which this ore is derived. The ^{208}Pb/^{204}Pb ratio for this sample is slightly lower than the common lead value, suggesting the source of the U is characterized by a low Th/Pb ratio relative to average continental crust.

The Denison and NUFCOR samples have ^{206}Pb/^{204}Pb and ^{207}Pb/^{204}Pb ratios that are somewhat higher than common Pb. This radiogenic Pb signature of the Denison "Dirt" ore and the NUFCOR ore derived from the Vaal Reef deposits reflect the higher U/Pb ratio (and corresponding U concentration), as well as ancient age of these ores relative to the Palangana ore. The two Denison samples and the suite of South African NUFCOR samples each form linear arrays between the radiogenic Pb produced by decay in the ore bodies and common terrestrial Pb values (Figures 9 and 10). This suggests that processing of the ore effectively removes the radiogenic Pb and adds common crustal Pb as contamination. This effect is particularly apparent in the South African NUFCOR suite of samples that form a linear array in ^{207}Pb/^{204}Pb space. Plots of ^{208}Pb/^{204}Pb versus either ^{206}Pb/^{204}Pb or ^{207}Pb/^{204}Pb are not linear. Instead the processing by-products and UOC have lower ^{208}Pb/^{204}Pb ratios than would be predicted by simple contamination of radiogenic Pb in the ore with common Pb derived from processing reagents. We do not fully understand this observation, but note that partial dissolution of the ore during the initial leaching steps could fractionate ^{208}Pb from the other isotopes if a Th bearing phase was preferentially dissolved relative to U bearing phases. This speculation may not be unrealistic given the fact that the most common Th bearing phase in many ore bodies are phosphates that easily dissolve in weak acids.

Table 15 Lead isotope analyses by MC-ICP-MS for Palangana Ore and Denison Ore and UOC(expanded uncertainty k=2)

Sample	$^{208}Pb/^{206}Pb$	Uncert.	$^{207}Pb/^{206}Pb$	Uncert.	$^{208}Pb/^{204}Pb$	Uncert.	$^{207}Pb/^{204}Pb$	Uncert.	$^{206}Pb/^{204}Pb$	Uncert.
Palangana Ore	1.99422	0.00017	0.813805	0.000071	38.2498	0.0054	15.6093	0.0022	19.1799	0.0031
Denison UOC	0.942802	0.000081	0.411199	0.000025	38.663	0.011	16.8623	0.0045	41.008	0.011
Denison Ore	1.32430	0.00011	0.553242	0.000048	38.6739	0.0054	16.1561	0.0023	29.2025	0.0046

Table 16 Lead isotope analyses by MC-ICP-MS (expanded uncertainty k=2)

Sample	$^{208}Pb/^{206}Pb$	Uncert.	$^{207}Pb/^{206}Pb$	Uncert.	$^{208}Pb/^{204}Pb$	Uncert.	$^{207}Pb/^{204}Pb$	Uncert.	$^{206}Pb/^{204}Pb$	Uncert.
Comminuted Ore	41.87	0.23	41.83	0.25	192.5	1.3	0.217525	0.00006	0.217289	0.000037
Cleared Leachate Solution	41.49	0.23	40.65	0.24	185.5	1.2	0.223753	0.000061	0.219184	0.000037
IX eluate	45.21	0.25	36.72	0.22	159.3	1.1	0.283720	0.000078	0.230476	0.000039
ADU Slurry	39.728	0.029	21.645	0.014	58.731	0.043	0.676261	0.000095	0.36854	0.00011
ADU Slurry	39.07	0.02	19.717	0.011	45.671	0.028	0.855310	0.00011	0.431756	0.000054
Filtered ADU	38.087	0.018	17.4177	0.0074	30.011	0.015	1.269090	0.00015	0.580382	0.000069
Calcined U_3O_8	37.945	0.018	16.0682	0.0068	20.502	0.011	1.850770	0.00022	0.783755	0.000093

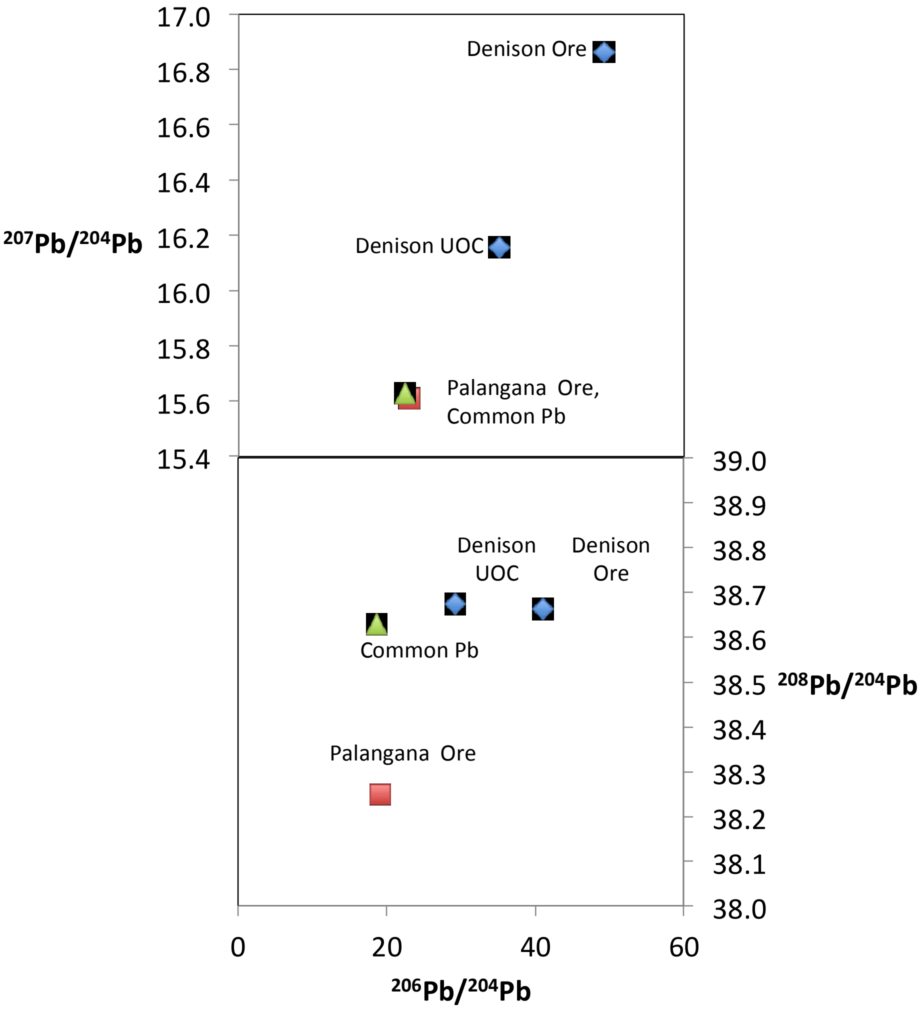

Figure 9 Pb isotopic ratios in the Denison samples fall on a linear array between the radiogenic Pb component in the Ore and common lead. The Pb isotope ratios of the Palangana ore is identical to common Pb.

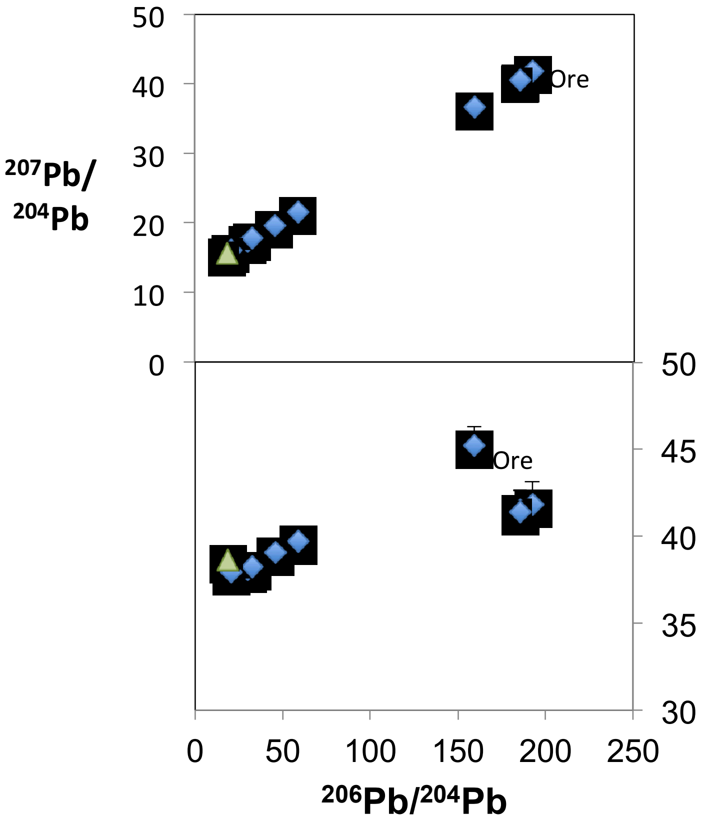

Figure 10 Pb-Pb plots for the South African NUFCOR Samples. The Pb isotopic compositions of the ore, UOC, and intermediate products from a linear array between the radiogenic lead in the ore and the accepted values for common terrestrial lead (Stacey and Kramers, 1971)

Strontium Isotopes:

Strontium isotopic ratios were measured for the paired ore/UOC samples and for all of the solid South African samples (Tables 17 and 18). The paired ore/UOC samples have vastly differing $^{87}Sr/^{86}Sr$ compositions, with variation well outside of analytical uncertainty. In the case of the Palangana Ore/Hobson UOC, the $^{87}Sr/^{86}Sr$ of the ore is well below the $^{87}Sr/^{86}Sr$ of the UOC. In contrast, the isotopic ratio of the Denison UOC is much higher than the $^{87}Sr/^{86}Sr$ of the Denison “Dirt” ore. The South African suite of samples shows a systematic decrease in $^{87}Sr/^{86}Sr$ throughout the processing steps, with the most significant decrease in the first leaching step (Figure 11). The results of the Sr isotopic measurements suggest that the strontium isotopic signature of a UOC does not reflect the isotopic composition of the ore from which it was derived. This is likely because the isotopic composition of the ore is determined by its mineralogy, particularly the abundance of clays that typically have high $^{87}Sr/^{86}Sr$ ratios. Differences in the Sr isotopic composition of the UOCs and ores mat therefore reflect the fact that are ores are produced by leaching of the ores rather than complete dissolution. Thus, the $^{87}Sr/^{86}Sr$ of the UOC reflects the isotopic composition of the leachable strontium in the ore. If radiogenic Sr in clays is not liberated in the leaching process, then the UOC will have significantly lower $^{87}Sr/^{87}Sr$ than the parent ore. Nevertheless, $^{87}Sr/^{86}Sr$ varies widely among UOCs, and while it is like to be marginally useful for tracing the sample back to the protolith ore, it is remains a useful parameter for distinguishing between UOCs of different origins.

Table 17 Strontium isotopic analysis by TIMS (expanded uncertainty k=2)

Sample	^{87}Sr/^{86}Sr	uncert.
Hobson UOC	0.708028	0.000030
Palangana Ore	0.709389	0.000030
Denison UOC	0.712487	0.000030
Denison "Dirt" Ore	0.710402	0.000030

Table 18 Strontium isotopic analysis by TIMS (expanded uncertainty k=2)

Sample ID	Sample Description	^{87}Sr/^{86}Sr	uncertainty	^{84}Sr/^{88}Sr	uncertainty
12850-14	Comminuted Ore	0.835095	0.000030	0.056498	0.000015
12850-01	Cleared Leachate	0.740026	0.000030	0.056511	0.000006
12850-11	ADU Slurry	0.720282	0.000030	0.056494	0.000002
12851-04	ADU Slurry	0.720254	0.000030	0.056497	0.000003
12581-07	Filtered ADU	0.720395	0.000030	0.056493	0.000002
12851-01	Calcined U3O8	0.720798	0.000030	0.056492	0.000002

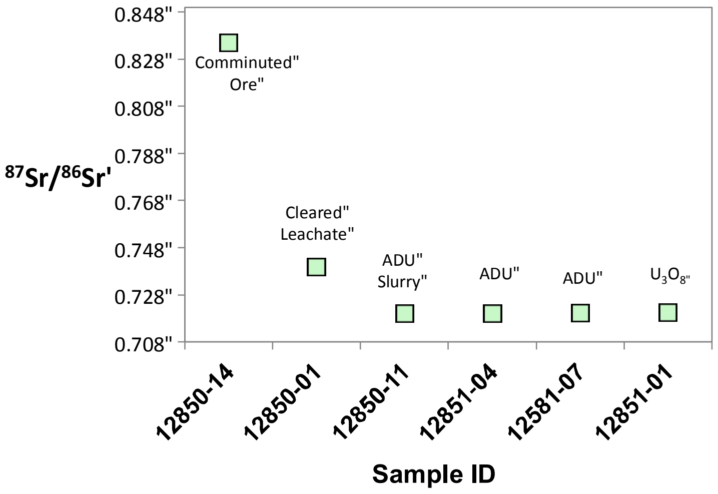

Figure 11 The strontium isotopic composition of the comminuted ore, UOC, and intermediate products from South African NUFCOR. The ^{87}Sr/^{86}Sr decreases substantially from the ore to the cleared leachate and then again between the leachate and the ADU precipitate. The two ADU samples and the U_3O_8 are isotopically similar but differ outside of analytical uncertainty.

Carbon, Sulfur, Nitrogen Concentrations and Stable Isotopes:

Carbon, sulfur and nitrogen concentrations for the South African NUFCOR samples are presented in Table 19. Nitrogen, sulfur, and carbon concentrations and isotopes were generally below detection limits in the Palangana Ore/Hobson UOC and Denison samples. Nitrogen and carbon concentrations are highest in the loaded solution and ADU samples; the calcined sample has significantly lower N and C concentrations. Carbon, nitrogen, and sulfur concentrations are highest in the reagents (12850-05, 12850-07 and 12850-09). Calcination effectively removes carbon and nitrogen from the final U_3O_8 product, but is less effective at removing sulfur from the UOC. Nitrogen isotopes were measureable in the cleared leachate, the reagents, and the UOC sample. The UOC isotopic ratio differs from the reagents outside of analytical uncertainty implying that calcination strongly fractionates nitrogen isotopes. Although carbon isotopes were only measurable in the ADU products, the three products (two ADU slurry samples and one dried ADU) are indistinguishable within analytical uncertainty. This implies that carbon isotopes may be consistent between UOCs sourced from the same location and could be an important forensic signature, although clearly the signature is lost following calcination. The observed $\delta^{15}N$ and $\delta^{13}C$ values are within the range typically observed in UOCs and uranium ores.

Table 19 Carbon, sulfur, and nitrogen concentrations by elemental analyzer, (expanded uncertainties k=2).

Sample ID	Sample Description	N wt. %	Uncert.	C wt. %	Uncert.	S wt. %	Uncert.
12850-01	cleared leachate solution	0.2	0.3	-0.06	0.16	0.630	0.18
12850-03	IX eluate	-0.11	0.06	-0.1	0.2	4.3	0.3
12850-05	loaded solution (OK liquor)	4.00	0.03	-0.12	0.110	4.230	0.12
12850-11	ADU Slurry - South Uranium Plant	1.837	0.005	0.062	0.009	0.81	0.04
12851-04	ADU Slurry-NUFCOR Plant	1.890	0.004	0.057	0.008	0.89	0.03
12581-07	*Filtered ADU*	1.658	0.005	0.053	0.009	1.57	0.04
12851-01	Calcined U_3O_8	0.054	0.004	-0.011	0.007	1.12	0.03
12850-07	Stripped solution (raffinate)	0.11	0.05	-0.06	0.2	2.9	0.3
12850-09	barren mother liquor	3.99	0.06	-0.11	0.16	4.0	0.2

Table 20 Carbon and nitrogen isotope data, (expanded uncertainties k=2).

Sample ID	Sample Description	δ^{15}N(air)‰	Uncertainty	δ^{13}C‰(VPDB)	Uncertainty
12850-01	cleared leachate solution	-0.54	0.14	null	null
12850-03	IX eluate	null	null	null	null
12850-05	loaded solution (OK liquor)	-2.05	0.14	null	null
12850-11	ADU Slurry - South Uranium Plant	null	null	-24.40	0.12
12851-04	ADU Slurry-NUFCOR plant	null	null	-25.24	0.12
12581-07	Filtered ADU	null	null	-24.65	0.17
12851-01	Calcined U_3O_8	4.6	0.2	null	null
12850-07	Stripped solution (raffinate)	null	null	null	null
12850-09	barren mother liquor	-2.06	0.2	null	null

Interpretation:

Note: Interpretations are technical judgments based upon current results.

Analysis of the results of the three sets of samples provides some insight into the behavior of trace elements and isotopes in uranium materials as the uranium is concentrated. The three sets of samples in this study are from three very different geological settings, and each uranium ore went through significantlydifferent uranium extraction processes. The first sample set (Palangana/Hobson) includes a low-grade uranium ore from a sandstone hosted roll-front deposit. The uranium was extracted through in-situ leaching and concentrated with ion exchange columns, and the final product is not calcined. The second set (Denison) is sourced from an unconformity type deposit. The uranium ore is removed via an open pit mine and concentrated by solvent exchange, and the final product is calcined. The third set is a suite from South Africa including uranium ore, UOC, and intermediate products from the uranium processing circuits at the AngloGold-Ashanti South Uranium Plant near Klerksdorm, North West and the NUFCOR Plant near Westonaria, Gauteng. The South African samples are sourced from three quartz pebble conglomerate deposits. The uranium was mined via underground techniques, gold was removed prior to uranium extraction and concentration. The uranium was concentrated by both ion exchange and solvent extraction, and the final product was calcined.

A surprising result from this comparison study is that the ^{234}U/^{238}U isotopic composition of the protolith ore is not necessarily preserved in the associated UOC. The ^{234}U/^{238}U isotopic ratios of the Palangana/Hobson pair and the South African ore/UOCs differ well outside of analytical uncertainty. In fact, the ^{234}U/^{238}U of the Palangana ore and Hobson UOC are each in the high and low extremes of ^{234}U/^{238}U ratios observed within the UOC database. Such dramatic shifts in U isotopic composition were unexpected, but can likely be explained by a combination of factors reflecting the increased mobility of ^{234}U relative to the other U isotopes during geologic U mobilization events and leaching of U ores during processing. In any case. although U isotopes are certainly useful for distinguishing between different UOCs, they do not necessarily constrain their protolith ores.

Strontium and Pb isotope ratios in UOCs are also significantly shifted from the composition of the protolith ores. Strontium can be shifted to either higher or lower values in the UOCs relative to the original ore, and the Sr isotope ratio of the UOC appears to reflect the Sr isotope composition of the U-bearing phases rather than the bulk ore composition. The direction and magnitude of the shift might reflect the amount of clay in the protolith ore sample.

The Pb isotope composition of the U ores often contains a radiogenic Pb component produced by the radioactive decay of ^{238}U, ^{235}U, and ^{232}Th. The associated UOC and UOC by products have compositions that approach those of common crustal lead indicating progressive contamination of the ore Pb with Pb from the processing stream. Thus, the UOC analyzed here have Pb isotopic compositions that are very similar to the common Pb value. Neither Sr nor Pb isotopes in UOCs are likely to be identical to the composition of the protolith ore, but both remain useful for distinguishing between UOCs. It is important to note that highly radiogenic Pb signatures can be a powerful discriminating characteristic for some UOCs. Another important finding is that although the Sr isotope ratios are dramatically different between the ore and the final products, the South African suite demonstrates that the ^{87}Sr/^{86}Sr are similar (though not identical) in the ADU and U_3O_8 samples produced over a period of a few weeks. This suggests that ^{87}Sr/^{86}Sr values from a single mine/mill operation may remain consistent over time.

Each of the processing regimes represented in the sample suites was effective at removing most of the trace element impurities. In each of the UOCs nearly every element was reduced significantly, although a few elements were concentrated in the UOCs. In the Hobson UOC, Na was not significantly reduced relative to other cations, whereas Se and Sn were actually slightly more concentrated in the UOC than in the original ore. In the Denison UOC, Na, Zr, and Mo were increased relative to the Denison “Dirt” ore. This likely reflects the addition of the elements during processing, or the fact that some elements partially follow U throughout the processing stream and are therefore not reduced in abundance.

Another interesting effect of the U concentration process is that rare earth elements can be fractionated from one another. In each of the UOCs, but particularly in the UOCs that were processed through ion exchange, the light REEs appear to have been more effectively removed than the heavy REEs. This can be observed in the normalized plots of elemental concentrations and also in the REE plots, showing depletion in LREE relative to HREE. It is possible that LREEs become fractionated from the heavy and middle REEs as a result of incomplete elution of the REEs on the ion exchange columns. This would explain why the effect is magnified in the two processing streams that employ ion exchange chromatography but not in the solvent-extraction-only circuit. In any case, this suggests that REE signatures may not be as effective a predictive signature as previously believed.

In conclusion, many of the isotopic and elemental signatures appear to be quite effective for discriminating between UOCs, but are unlikely to directly reflect the protolith ore.

For this reason, directly comparing ore and UOC data may not be appropriate for attributing UOC to a particular mine. However, comparing UOC signatures remains a useful tool for distinguishing between UOCs of different origins, and the best approach appears to be developing a robust database of UOC elemental and isotopic characteristics.

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