Report on
Initial Direct Soil Leaching Experiments
Using Post-Detonation Debris

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Introduction

A key challenge of nuclear forensics is reducing the time and manpower effort required to measure nuclear debris compositions. The overall motivation for this work is to explore development of a robust, automated system that can be used to concurrently analyze several elements/isotopes associated with the forensic signature of nuclear materials. The primary focus of this research has been to methodically investigate if rapid partial leaching of post-detonation debris can yield usable elemental and isotopic information for interpretation.

The unique requirements of post-detonation nuclear forensics have not been fully adapted to or fully incorporated contemporary chemical separation techniques. Challenges include addressing the range of material matrices or mixed fission product and actinide compositions and concentrations that might be encountered. These include, but are not limited to, puddle melt glass, urban debris, seawater, air filters, iron-rich urban debris, asphalt, and silica sand. Separation of these elements and their subsequent measurement is a key element of related laboratory analysis activity. Existing practices at LLNL rely on proven but time-consuming and labor intensive processes. Significant time and labor savings are possible in chemical separations, however, if rapid processing methods can be adapted to post-detonation debris.

Development of a simple and reliable leaching technique could shorten analytical times and would be useful as a field deployable method for the preliminary characterization of actinide isotopic ratios in soils. Measurement of isotopic ratios in the field using modern mass spectrometry capabilities such as Inductively Coupled Plasma Mass Spectrometry (ICP-MS) is desirable, taking advantage of the extended range of isotopic systems measureable using such instruments. Sample introduction to these types of mass spectrometry instruments requires partial leaching or full dissolution of a sample to remove isobaric (same mass) interferences, and, in some cases, to concentrate the elements(s) of interest. To develop a field-deployable mass spectrometry capability, therefore, automated and robust leaching of likely debris samples (ranging from silicates and oxides to metals and urban materials such as concrete and asphalt), followed by separation/purification through cation exchange column chemistry is necessary. In a post-detonation environment, analysis of melt glasses via rapid leaching and ICP-MS could be a viable route to the same goal.

This report presents initial leaching experiments on 'uncontaminated' soils, as well as data from melt glass from a single nuclear weapons test. Samples were characterized by gamma spectrometry, then aliquoted for rapid leaching experiments. Experiments were conducted using

two different rapid acid treatments to leach the soils. Following leaching, the leachate solutions were analyzed by ICP-MS to determine if U isotopic composition. We present these data to address the question as to whether or not rapid (~1 hr) leaching techniques have the potential to yield meaningful U isotopic compositions, without the need for a complete (time consuming) sample dissolution and separation.

Experimental Methods

Four surface soil samples were collected at the Nevada Test Site away from areas directly affected by weapons testing and fallout. Soils were analyzed by gamma spectroscopy to determine ^{235}U concentrations (Table 1). Two aliquots, 3 g each, were removed from each of these samples for sample leaching. The ^{235}U concentrations in each aliquot were extrapolated from the gross sample concentration. For each soil, one aliquot was then leached with 8M HNO_3 and the other aliquot was leached using a 2% HF and concentrated HNO_3 mixture. Both reagents were added to the aliquots at a ratio of 10 ml/g of sample at room temperature in polypropylene vials. Leach times were 1 hour at room temperature, with manual mixing. Following leaching, the acid solutions were separated from the solids by vacuum filtration using 0.1 um pore size polypropylene filters. The 8M HNO_3 leachates were volumetrically diluted by a factor of 10 using a 5% HNO_3 solution containing a ^{233}U internal standard. The 2% HF and concentrated HNO_3 leachates were volumetrically diluted by a factor of 20 using a 5% HNO_3 solution containing the same ^{233}U internal standard.

Sample	Mass (g)	Estimated ^{235}U (atoms/g)	Estimated ^{235}U (atoms/sample)
Soil 22 -A	3.0108	1.5E+14	4.5E+14
Soil 22 -B	3.0112	1.5E+14	4.5E+14
Soil 46 -A	3.0042	4.8E+13	1.5E+14
Soil 46 -B	3.0266	4.8E+13	1.5E+14
Soil 50 -A	3.0297	9.0E+13	2.7E+14
Soil 50 -B	2.9981	9.0E+13	2.7E+14
Soil 64 -A	3.0459	8.2E+13	2.5E+14
Soil 64 -B	3.0288	8.2E+13	2.5E+14
Melt Glass - Solid	0.499	2.6E+16	1.3E+16
Melt Glass - Crushed	0.4962	3.4E+16	1.7E+16
Melt Glass - Powdered	0.5667	2.5E+16	1.4E+16
Reagent Grade SiO_2 -A	3.018	N/A	N/A
Reagent Grade SiO_2 -B	2.9931	N/A	N/A
Reagent Blank -A	N/A	N/A	N/A
Reagent Blank -B	N/A	N/A	N/A
U005a Standard	N/A	N/A	N/A

Table 1: Sample masses and ^{235}U concentrations measured by gamma spectroscopy. The A and B samples represent duplicate measurements of the same sample. While absolute errors were not quantified, measurement reproducibility was excellent.

Three samples of melt glasses originating from a uranium-fueled surface test at the Nevada Test Site, from a nearby location to the 'uncontaminated' soils (and therefore having a similar soil composition/chemistry), were also selected for study. The melt glass aliquots each contained 0.5 g of glass, and were selected have a comparable grain size (3.35 mm) to the 'uncontaminated' soils. Preliminary ^{235}U concentrations of each melt glass sample was determined by gamma spectroscopy. The surface area of the melt glass samples was then altered for two of the three

melt glass leaching experiments. One melt glass sample was powdered into a fine dust by grinding in a ball mill for two minutes using stainless steel grinding balls and an acrylic grinding vessel. The third sample was crushed into 0.5-2 mm grains by manually shaking the glass, using the same stainless steel balls and acrylic vessel used in the ball mill preparation, for 30 second. The third was left intact, with its original surface. The three melt glass samples [solid (3.35 mm), crushed (0.5-2 mm) and powdered (fine)] were then leached using similar procedures to those applied to the 'uncontaminated' soils. For each melt glass sample, one aliquot was leached with a 8M HNO_3 mixture. The reagents were added to the aliquots at a ratio of 10 ml/g of sample at room temperature in polypropylene vials. Leach times were 1 hour at room temperature, with manual mixing. Following leaching, the acid solutions were separated from the solids by vacuum filtration using 0.1 um pore size polypropylene filters. The 8M HNO_3 leachates were volumetrically diluted by a factor of 10, using a 5% HNO_3 solution containing the same ^{233}U internal standard. Only minimal dissolution of material was observed, and was confirmed by leachate analyses. Thus, the same samples were then used for 2% HF with concentrated HNO_3 leaching experiments, rather than introducing virgin material. The 2% HF with concentrated HNO_3 leachates were volumetrically diluted by a factor of 20, using a 5% HNO_3 solution containing a ^{233}U internal standard. Table 1 contains the complete sample list.
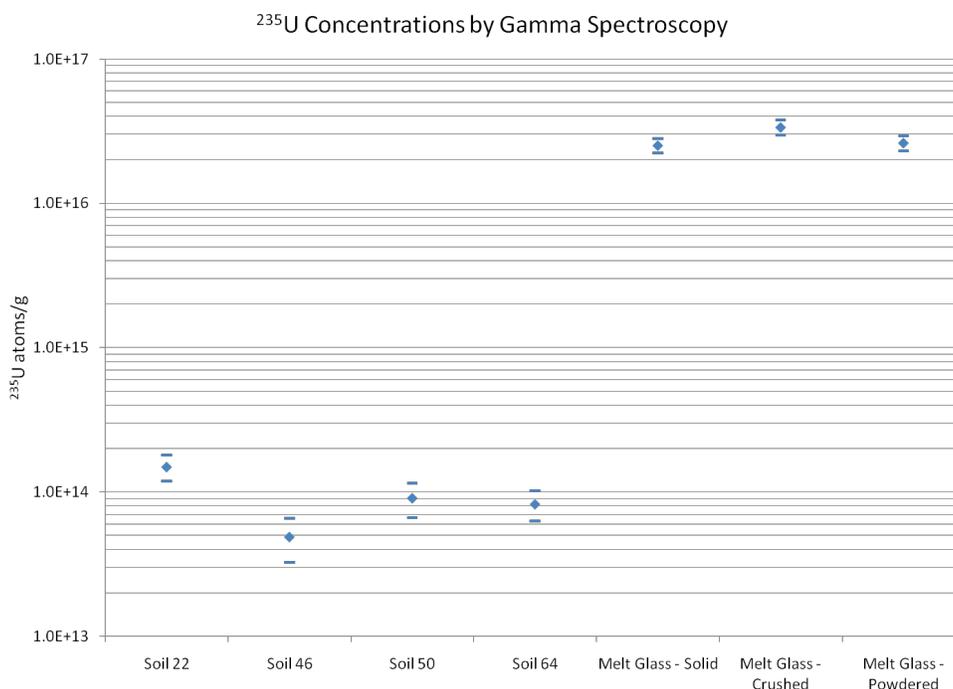
Figure 1: Semi-log plot of ^{235}U concentrations in the soil samples and melt glass samples determined by gamma spectroscopy. Soil concentrations are ~10^{14} atoms/g of ^{235}U, while melt glass concentrations are ~10^{16} atoms/g of ^{235}U. Errors are derived from the averages of the replicate analyses (1 standard deviation).

Collection of the ICP-MS data from the 11 samples (8 uncontaminated soil leachates and 3 melt glass leachates) was performed during a single experimental run using a Thermo X7 quadrupole ICP-MS instrument at LLNL. Analysis of reagent blanks was performed at the same time using two standards (the U005a standard, and a reagent grade SiO_2 with an unknown U-isotopic composition, selected for improved matrix match). The standards leached using the same

materials and methods as used in the soil samples. Data were acquired with peak jumping scans at masses 232 - 239 and 245 (background), and using a survey scan covering 5 – 259 AMU, for each sample. ICP-MS data for masses 235, 236 and 238 are presented in Table 2. As ICP-MS samples were prepared volumetrically, no absolute U concentration values are reported, and uranium concentrations instead rely on initial gamma spectrometry analyses. Complete microwave dissolution of one soil sample and one melt glass sample were also done to obtain the full isotopic values of the samples for comparison with the leachates.

Results and Discussion

Gamma-spectrometry analyses yield ^{235}U concentrations on the order of $\sim 10^{14}$ atoms/g for all soil samples. The melt glasses, in comparison, yield concentrations two orders of magnitude greater ($\sim 10^{16}$ atoms/g of ^{235}U; see Table 1, Figure 1).

Leaching of soil samples using the 2% HF with concentrated HNO_3 treatment, as well as the 8M HNO_3 treatment, is effective at liberating enough U from the soil matrix to make statistically sound measurements of the $^{238}U/^{235}U$ of the samples by ICP-MS (Table 2). The measured $^{238}U/^{235}U$, however, varies with leach treatment and introduced sample form (solid, crushed and powdered).
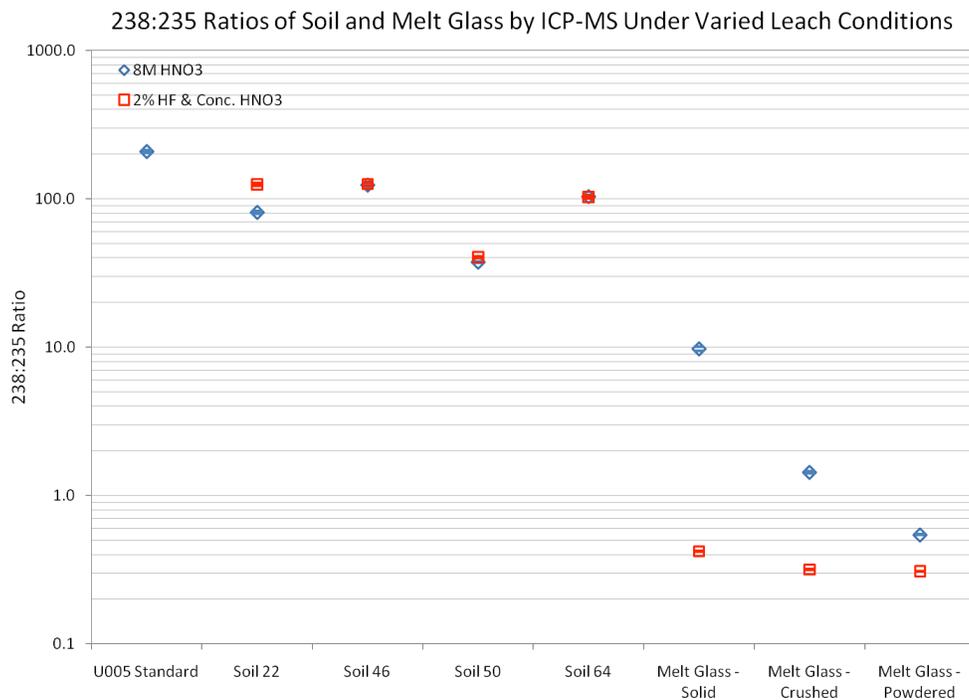
Figure 1: $^{238}U/^{235}U$ ratios for the 8M HNO_3 and the 2% HF with concentrated HNO_3 leaching experiments. The U005 standard has a reported $^{238}U/^{235}U$ value of 200, the observed vale was 208 ± 4. Errors are generally within the symbols, and are 1σ.

The 2% HF with concentrated HNO_3 leachates from the soils contain 13-56% more U than the 8 M HNO_3 leachates (Table 2), resulting in the reduction of uncertainties for the 2% HF with concentrated HNO_3 system. The $^{238}U/^{235}U$ ratios (Figure 1) are reproducible within errors for both reagent systems in 3 of the 4 soil samples. Soil 22, when leached using the 2% HF with

concentrated HNO_3 solution, yields an increased ^{238}U signal by 43%, while the ^{235}U yield is increased by only 13%, relative to the 8M HNO_3 leach, resulting in a fractionated isotopic ratio. It cannot be determined from these experiments whether this apparent isotopic fractionation is due to some introduced variation between aliquot 22-A and 22-B, or if the 2% HF with concentrated HNO_3 solution is able to access a soil component rich in ^{238}U not leached by 8M HNO_3, but present only in this soil.

Sample	Leaching Reagent	Counts @ 235 AMU	Counts @ 236 AMU	Counts @ 238 AMU	$^{236}U/^{235}U$	$\pm 1\sigma$	$^{238}U/^{235}U$	$\pm 1\sigma$
Soil 22 -A	8M HNO_3	1765	13	142827	0.0076	0.0021	80.9	1.9
Soil 22 -B	2% HF, conc. HNO_3	2032	3	254261	0.0013	0.0008	125	3
Soil 46 -A	8M HNO_3	810	0	100164	^{236}U n.d.	N/A	124	4
Soil 46 - B	2% HF, conc. HNO_3	1432	3	180350	0.0019	0.0011	126	3
Soil 50 -A	8M HNO_3	5763	11	215535	0.0019	0.0006	37.4	0.5
Soil 50 -B	2% HF, conc. HNO_3	8319	15	336295	0.0018	0.0005	40.4	0.4
Soil 64 -A	8M HNO_3	1349	2	139498	0.0015	0.0010	103	3
Soil 64 - B	2% HF, conc. HNO_3	3133	0	322446	^{236}U n.d.	N/A	103	2
Soil - complete	**2% HF, conc. HNO_3**	**4906**	**19**	**161175**	**0.0040**	**0.0010**	**32**	**8**
Melt Glass - Solid	8M HNO_3	1011	4	9847	0.0040	0.0020	9.74	0.32
Melt Glass - Solid	2% HF, conc. HNO_3	194555	929	81553	0.0048	0.0002	0.419	0.002
Melt Glass - Crushed	8M HNO_3	5516	24	7910	0.0044	0.0009	1.43	0.03
Melt Glass - Crushed	2% HF, conc. HNO_3	486343	2315	154245	0.0048	0.0001	0.317	0.001
Melt Glass - Powdered	8M HNO_3	55247	293	29997	0.0053	0.0003	0.543	0.004
Melt Glass - Powdered	2% HF, conc. HNO_3	836652	4000	258287	0.0048	0.0001	0.309	0.001
Glass - complete	**2% HF, conc. HNO_3**	**862799**	**4300**	**169030**	**0.0050**	**0.0001**	**0.196**	**0.002**
Reagent Grade SiO_2 -A	8M HNO_3	11	0	1058	^{236}U n.d.	N/A	95.6	28.9
Reagent Grade SiO_2 - B	2% HF, conc. HNO_3	37	1	3453	0.0365	0.0322	94.5	15.7
Reagent Blank -A	8M HNO_3	7	0	797	^{236}U n.d.	N/A	116	44
Reagent Blank -B	2% HF, conc. HNO_3	295	1	5568	0.0045	0.0039	18.9	1.1
U005a Standard		2235	19	464876	0.0084	0.0019	208.0	4.4

Table 2: ICP-MS data for masses 235, 236 and 238 by sample and reagent system. Errors are 1σ. The certified values for U005a are $^{238}U/^{235}U = 196.46 \pm 0.12$ and $^{236}U/^{235}U = 0.00233 \pm 0.00002$. 'Complete' samples indicate a complete microwave dissolution run by ICP-MS.

Natural $^{238}U/^{235}U$ uranium isotopic ratios were not observed in any of the soils using these leaching treatments. Instead, all soils suggest some degree of ^{235}U enrichment. This may be a result of fractionation from the leaching process, but may also reflect the influence of contamination of the soils from weathering and transport of nuclear test debris with non-natural uranium isotopic composition at the Nevada Test Site. The U005a standard yielded a $^{238}U/^{235}U$ 208 ± 4.4, just outside of errors of the certified value. Both the $^{238}U/^{235}U$ and $^{236}U/^{235}U$ suggest some enhancement of the ^{235}U signal inconsistent with mass fractionation, but possibly reflecting a source of systematic error. Corrections were not made for potential hydride interferences. The leachate analyses of the homogeneous SiO_2 standard yielded well-reproduced, non-natural $^{238}U/^{235}U$ compositions of ~95. While the true uranium isotopic composition of the SiO_2 material is not known, the well-replicated precision confirms that the two reagent systems do not *a prioi* cause or introduce fractionation of uranium isotopes in silicate-dominated systems.
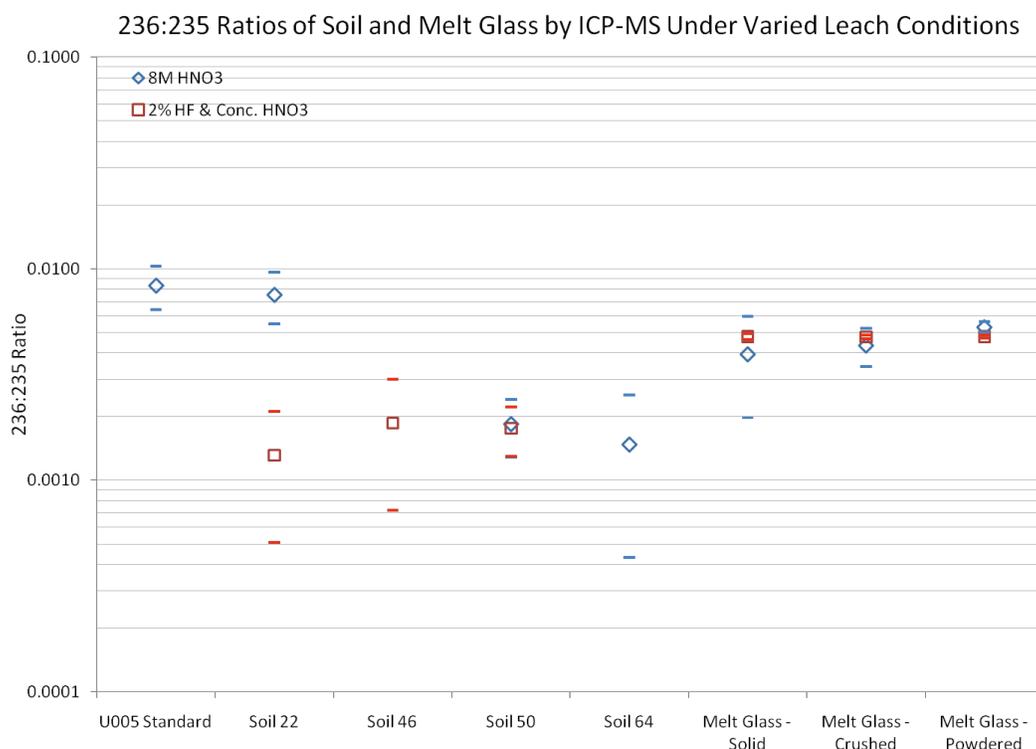
Figure 2: Melt glass samples yield a uniform $^{236}U/^{235}U$ ratio within errors regardless of the surface area of the leached sample. The large uncertainties in the $^{236}U/^{235}U$ ratios in the soils are due to small ^{236}U signals in the soils and from the 8M HNO_3 leached melt glass samples.

Unlike the soil samples, large variations are observed in the measured melt glass $^{238}U/^{235}U$ ratios across both reagent systems, and as a function of the physical form of the introduced sample (solid, crushed and powdered, see Figure 1). A decreasing $^{238}U/^{235}U$ ratio is observed in the 8M HNO_3 leaching experiments as a function of increased surface area of the melt glass samples. Such a trend is highly suggestive of a bimodal mixing with surfacial natural-composition uranium dominating the most easily leached sites within the sample. The observed trends imply that the ^{235}U fuel component preserved the melt glass is not the dominant component being leached from the melt glass over these time scales and/or acid temperatures.

The same trend of decreasing measured $^{238}U/^{235}U$ ratios is observed in the 2% HF with concentrated HNO$_3$ data, although the effect is not as dramatic as that observed with the 8M HNO$_3$ system. In the case of the 2% HF with concentrated HNO$_3$ treatment, the crushed melt glass and powdered melt glass yield identical, minimum $^{238}U/^{235}U$ ratios within errors, and significantly lower that the ratio realized from the powdered melt glass 8M HNO$_3$ experiment. Both reagent systems demonstrate that increasing the surface area of the melt glass will provide a better representation of the gross $^{238}U/^{235}U$ ratio. The observed trends with increased surface area likely reflect a decreasing contribution from a background of natural isotopic composition U. The 2% HF with concentrated HNO$_3$ data, however, suggest that the primary $^{238}U/^{235}U$ component has been accessed, and that the background contribution from surficial natural uranium has been minimized.

The $^{236}U/^{235}U$ isotopic ratios are plotted by sample in Figure 2. Precise determination of the $^{236}U/^{235}U$ ratio in the soil samples using either reagent system is difficult due to the low to absent ^{236}U concentration in the soil samples. This is not the case for the $^{236}U/^{235}U$ ratios in the melt glass samples, where the both the 8M HNO$_3$ and the 2% HF with concentrated HNO$_3$ leaching experiments yield measurable ^{236}U signals.
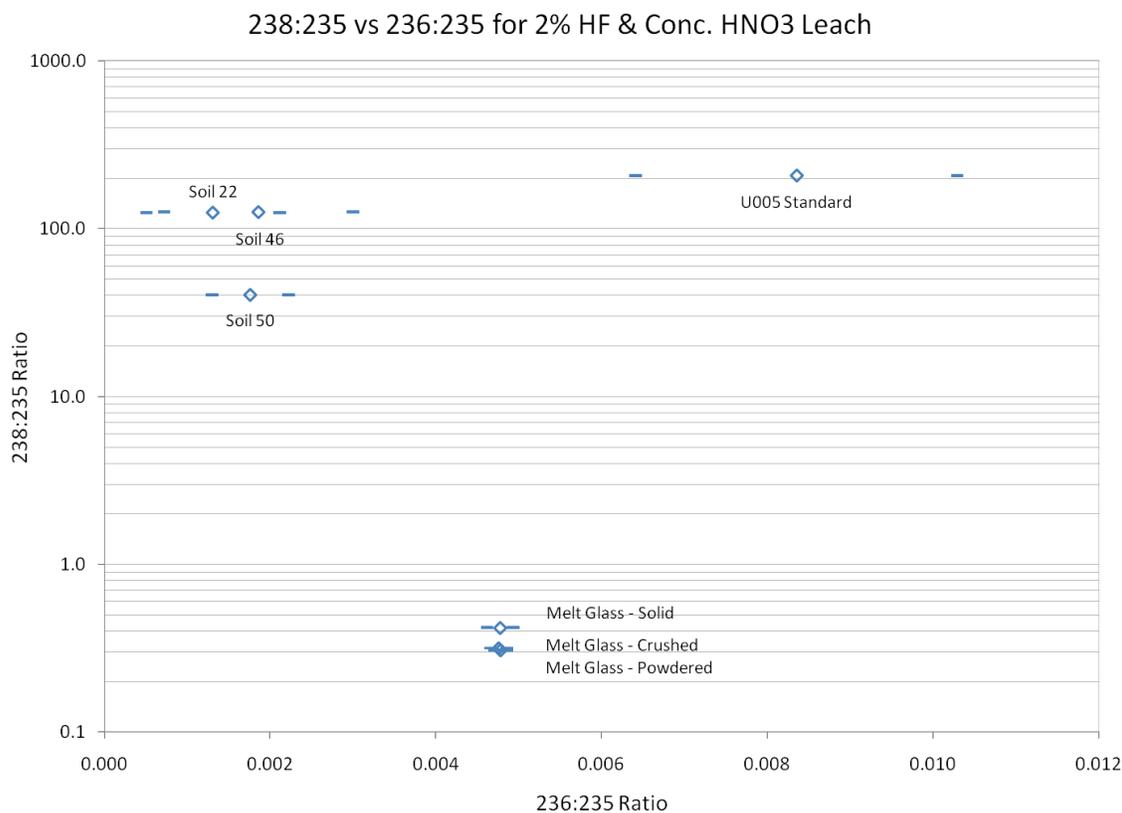
Figure 3: Semi-log $^{238}U/^{235}U$ versus $^{236}U/^{235}U$ mixing curve for three of the soil samples and all of the melt glasses leached by 2% HF and concentrated HNO3. The horizontal bars represent the uncertainty in the $^{236}U/^{235}U$ values, the $^{238}U/^{235}U$ uncertainties are captured within each marker. Errors are 1σ.

All melt glass leachates yield identical $^{236}U/^{235}U$ ratios within 2σ errors (Table 2). A significant difference is the total amount of ^{235}U, ^{236}U and ^{238}U in the 8M HNO$_3$ leach treatment relative to the 2% HF with concentrated HNO$_3$ treatment, however, resulted in comparatively larger error

bars in the 8M HNO$_3$ leachate analyses. Melt glass leached using 2% HF with concentrated HNO$_3$ yielded a ^{236}U/^{235}U ratio of 0.0048 ± 0.0001 across 3 samples, showing that the presence of ^{236}U signal is strongly correlated with ^{235}U.

Comparison of the total U signal (^{235}U+^{236}U+^{238}U) produced by the leaching of soils compared to that from the melt glasses, when leached with 2% HF with concentrated HNO$_3$, suggests that, although the isotopic compositions differ, the same order of magnitude amount of U is liberated (Table 2). The small ^{236}U signal in the soil samples results in ^{236}U/^{235}U ratios which approach zero with large uncertainties, are due to the isotopic distribution of U in the soil rather than a by-product of a diminished total U signal.

A semi-log plot of the ^{238}U/^{235}U relative to the ^{236}U/^{235}U ratios for the 2% HF with concentrated HNO3 leach samples (Figure 3) shows that the soil and melt glasses form two populations, easily distinguished from each other. This is not surprising, as ^{236}U is nearly absent in natural samples, and tends be present in samples where ^{235}U can have undergone significant neutron capture, such as materials derived from irradiated and/or fissioned uranium. The 'uncontaminated' soils also suggest the presence of a minor, non-natural uranium component, despite having been sampled from the subsurface, away from any known surface fallout plumes. Since the precise point of origin of the NTS soils is not known relative to the melt glass, extrapolating a mixing curve specific to this test shot may not be possible.

Conclusions and Recommendations
Fast leaching of soils with 8M HNO$_3$ may be sufficient for a preliminary determination of whether or not an enriched ^{235}U component is present in debris, but does not report the true ^{238}U/^{235}U value, as given by the full microwave dissolution. Crushed samples do, however, allow more rapid access of the primary uranium component. The times (1 hour) and temperatures (~32° C) explored, however, show that a rapid leaching approach using 8M HNO$_3$ is not sufficient to determine a reliable preliminary ^{238}U/^{235}U ratio, regardless of the introduced form of the sample.

The addition of HF to the leaching procedure, as explored using the 2% HF with concentrated HNO$_3$ leach samples, significantly increases the yield of uranium from the sample. These analyses suggest that this approach is significantly enhanced if the sample surface area is increased (crushed) prior to rapid leaching. Measurement of the bulk isotopic composition of the melt glass from a complete dissolution provides a comparison of the 'real' uranium isotopic composition of the fallout, and shows no combination of 2% HF with concentrated HNO$_3$ leaching of the crushed and powdered samples from this set of experiments realized these values within errors.

In practical terms, these data suggest that the use of HF is required to access the dominant uranium component in melt glass, and it is recommended that the samples be crushed or powdered to optimize the leaching procedure. Leach periods may need to be extended beyond 1 hour, though these preliminary data suggest that 1 hour is sufficient if a simple crushing precedes the leach step. If a sample of pure melt glass is available, we conservatively predict that sample masses as small as 25 mg are adequate to determine ^{238}U/^{235}U and ^{236}U/^{235}U ratios to better than 5%, including all propagated errors, assuming a ^{235}U loading of 10^{16} atoms/g. While not

providing true ratios, such a measurement would clearly establish the presence of enriched material.

As a proof of concept, these experiments demonstrate that fast leaching and ICP-MS analysis can be a useful tool for the preliminary analysis of actinide isotopic ratios in soils and melt glass. To validate these data and establish operational limits, additional experiments need to be performed. Coupled leaching and complete dissolution experiments on similar samples should be pursued to determine if the isotopic ratios from the leaching process are representative of the isotopic ratios in the soil. The leaching process also should be tested against Pu and mixed Pu/U systems to determine if the dissolution rates of Pu and U are different, and if they are, to determine a leaching period and set of reagents sufficient for all actinides of interest.