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Title: Spatially-Resolved Analyses of Aerodynamic Fallout from a Uranium-Fueled Nuclear Test

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Spatially-Resolved Analyses of Aerodynamic Fallout from a Uranium-Fueled Nuclear Test

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Highlights

- We measured the spatial distribution of U isotopes, major elements, and radioactivity in five glassy fallout spherules
- We used secondary ion mass spectrometry, electron microscopy, x-ray spectroscopy, and autoradiography
- In two spherules, the $^{235}\text{U}/^{238}\text{U}$ ratio is heterogeneous and correlated with major elements
- In two spherules, the $^{235}\text{U}/^{238}\text{U}$ ratio is approximately homogeneous
- These results reflect variable mixing between fallout spherules and between U from the device and the soil and allude to possible formation processes

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Abstract

Five silicate fallout glass spherules produced in a uranium-fueled, near-surface nuclear test were characterized by secondary ion mass spectrometry, electron probe microanalysis, autoradiography, scanning electron microscopy, and energy-dispersive x-ray spectroscopy. Several samples display compositional heterogeneity suggestive of incomplete mixing between major elements and natural U ($^{238}\text{U}/^{235}\text{U} = 0.00725$) and enriched U, exhibiting U isotopic heterogeneity with $0.02 < ^{235}\text{U}/^{238}\text{U} < 11.84$ among all five spherules and $0.02 < ^{235}\text{U}/^{238}\text{U} < 7.84$ within a single spherule. In two spherules, the $^{235}\text{U}/^{238}\text{U}$ ratio is correlated with major element composition, consistent with the agglomeration of chemically and isotopically distinct molten precursors. Two samples are nearly homogeneous with respect to composition and uranium isotopic composition, suggesting extensive mixing possibly due to experiencing higher temperatures or residing longer in the fireball. Linear correlations between $^{234}\text{U}/^{238}\text{U}$, $^{235}\text{U}/^{238}\text{U}$, and $^{236}\text{U}/^{238}\text{U}$ ratios are consistent with two-component mixing, which is used to illustrate the extent of mixing between natural and enriched U end members.

1. Introduction

There is renewed interest in post-detonation glassy fallout formed during surface and near-surface nuclear explosions (Parekh et al., 2006; Eby et al., 2010; Fahey et al., 2010; Belloni et al., 2011; Bellucci et al., 2012; Cassata et al., 2014; Eppich et al., 2014; Sharp et al., 2014). During the era of above ground nuclear testing, fallout analyses focused on understanding device performance and how radioactivity spread post-detonation. Techniques for analyzing fallout on small spatial scales were generally limited to methods such as autoradiography to image the distributions of fission and activation products (Adams et al., 1960). Today, using modern microanalytical techniques, spatially-resolved analyses of post-detonation fallout from historic nuclear tests can provide much more information on the distribution of stable and long-lived radioactive isotopes with the goal of a more comprehensive

understanding of fallout formation, such as improved constraints on formation mechanisms, timescales, and temperatures (Cassata et al., 2014; Eppich et al., 2014).

Glassy fallout forms when a nuclear device is detonated on or near the Earth's surface. Surface detonations melt large masses of environmental material (e.g., soil), which may remain in place or be swept into the nuclear fireball. In both cases, the molten material may interact with device components, fission and activation products, and unfissioned fuel (collectively 'device debris'; Brode, 1968; Glasstone and Dolan, 1977). As the fireball cools below the melting point of the surrounding material, device debris becomes trapped within a fused glassy matrix, forming glassy fallout. Because the mass of melted environmental material is much greater than mass of the device, the major element composition of these glasses is largely reflective of the local geology and/or emplacement environment and device debris is present in trace quantities (Adams and O'Connor, 1957; Miller, 1964).

There are two main morphological classes of glassy fallout, often referred to as ground glass and aerodynamic glassy fallout. Ground glass usually exhibits a glassy surface and compositional or morphological variations with depth, often transitioning to unmelted soil underneath (Eby et al., 2010). This is consistent with either in-situ melting of soil and/or molten material being swept into the fireball and raining back down onto the soil below (Hermes and Strickfaden, 2005). In contrast, aerodynamic glassy fallout (also known as fallout beads or spherules) usually appears glassy throughout and exhibits spheroidal, near-spheroidal, or dumbbell shapes, consistent with fusing while still aloft (Miller, 1960; Crocker et al., 1965; Tompkins et al., 1970; Fig. 1). Aerodynamic glasses often have smaller glassy spheres attached to their surfaces, consistent with growth or formation by the collision and subsequent mixing of molten droplets within the fireball (Miller, 1964; Stewart, 1956). For aerodynamic fallout, the cooling timescale depends on device yield, but is estimated (Glasstone et al., 1977; Izrael, 2002) and measured to be on the order of seconds (Cassata et al., 2014). Few previous studies have focused specifically on aerodynamic fallout glasses, but these objects are of particular interest due to their elevated concentrations of residual fuel and fission and activation products (Mackin et al., 1958; Gostic et al., 2012; Eppich et al., 2014). How direct device components distribute themselves within aerodynamic fallout, particularly in the case of U-fueled devices, remains unanswered.

Ground glass from the Trinity test, or trinitite, has been extensively studied over the past decade (Parekh et al., 2006; Eby et al., 2010; Fahey et al., 2010; Belloni et al., 2011; Bellucci et al., 2012; Bellucci et al., 2013; Wallace et al., 2013; Bellucci et al., 2014; Sharp et al., 2014). These studies demonstrate that trinitite is a compositionally heterogeneous mixture of completely melted, partially melted, and relic minerals found in the local geology with the glassy and eddied portions of the mineral containing most of the unfissioned Pu fuel and fission products. Analyses of trinitite have yet to be compared with observations of aerodynamic fallout from Trinity (called trinitite beads) or other nuclear tests.

In contrast to recent studies characterizing ground glass from the Pu-fueled Trinity test, this study characterizes aerodynamic fallout glass from a U-fueled device. We characterize the spatial distribution of unfissioned U fuel within glassy fallout spherules from a uranium-fueled test using secondary ion mass spectrometry (SIMS) combined with scanning electron microscopy/energy-dispersive x-ray spectroscopy (SEM/EDS), electron probe microanalysis (EPMA), and autoradiography. For each spherule, we measured the extent of uranium isotopic heterogeneity, major element composition, and radioactivity and correlated these observations with spatial locations within individual spherules. We quantify the extent of mixing by assuming two-component mixing between uranium from the soil and/or device and enriched uranium from the device and calculating the relative contribution of each end member to each U isotopic measurement.

2. Materials and methods

2.1 Fallout spherules

Five, millimeter-size fallout spherules were selected from soil collected from the site of a historic, uranium-fueled, near-surface nuclear test. The soil samples were collected about 120 meters from ground zero along the path of the fallout plume. Glassy fallout is easily identifiable in soil collections due to its smooth surface morphology and aerodynamic shape (Fig. 1). The spherules were isolated from sieved soils by visual inspection and handpicked under an optical microscope, then were weighed and photographed. Each spherule was mounted in epoxy and polished to expose an interior surface close to the mid-plane. Samples were coated with ~10-20 nm of carbon to prevent charging and characterized by SEM/EDS, EPMA, autoradiography, and SIMS.

[Figure 1 —Optical images of size-sorted fallout (left) showing distinct dark glassy aerodynamic shapes mixed with soil fragments, and an isolated piece of aerodynamic fallout glass (right). The bright artifact in the center of the isolated aerodynamic fallout glass is the ring light from the optical microscope, which also highlights the high degree of symmetry in these objects.]

The selected aerodynamic fallout samples range in diameter from 1.3-2.4 mm and in mass from 2.5-14.5 mg (Table 1). They appear light to dark green in color and are optically translucent and glossy. Vesicles are visible within the volume of the glasses.

[Table 1 — Fallout spherule labels, masses, and average diameters.]

2.2 Experimental methods

2.2.1 SEM, EDS, and EPMA

Backscattered electron images of the samples were taken using an FEI Inspect-F SEM equipped with an AMETEK EDAX Apollo XL Si drift energy-dispersive x-ray spectrometer. The SEM was operated at an accelerating voltage of 20 kV with a beam current of ~1.5 nA.

Elemental maps and major element compositions were determined with a JEOL JXA-8200 electron probe equipped with five wavelength-dispersive spectrometers, and a JEOL energy-dispersive x-ray spectrometer. X-ray intensities were converted to concentrations using CITZAF (Armstrong, 1995). The EPMA was operated with a 15 kV accelerating potential, 5 nA of probe current and a 2 μ m beam diameter. The following silicate and oxide standards were used: orthoclase (for Si, Al, K), Fe_2O_3 (for Fe), spessartine (for Mn), rutile (for Ti), diopside (for Ca), albite (for Na), and MgO (for Mg). The samples were analyzed for major element composition in rectangular arrays with 30-100 spot analyses per sample. Regions adjacent to vesicles, cracks or pits that resulted in element concentrations of less than 98 wt.% or greater than 102 wt.% were excluded.

2.2.2 Sample autoradiography

To obtain the autoradiographs, the samples were placed onto a photo-phosphor imaging plate for 34 hours inside a light-blocking tent. All five samples were imaged together on the same plate for the same length of time. The plate was developed and the autoradiograph images digitized using a GE Typhoon 7000 scanner at a spatial resolution of 50 μ m/pixel. The autoradiographs record the distributions of β^- activity and near-surface α activity (respective mean free paths of ~1 cm and ~10 μ m in silicates). Autoradiographs of these samples are dominated by β^- activity because of the low specific activity of U in these samples. The fission products ^{137}Cs and ^{90}Sr are the dominant sources of β^- radioactivity in fallout samples more than several decades old and are likely the major contributors of β^- radioactivity in these samples. In addition, the decay of ^{152}Eu and ^{154}Eu has been measured in similar glassy fallout spherules (Gostic et al., 2012).

2.2.3 Spatially-resolved U isotope measurements

Spatially-resolved U isotope ratios were measured by SIMS in two separate analytical sessions, one at Lawrence Livermore National Laboratory (LLNL) using a modified Cameca ims-3f SIMS instrument to analyze four of the five spherules (U1A was not analyzed at LLNL), and one at Los Alamos National Laboratory (LANL) using a Cameca ims-1280 SIMS to analyze all five spherules. The LLNL analyses measured the $^{235}\text{U}/^{238}\text{U}$ ratio on four spherules and U concentrations on two spherules (U3 and U4), while the LANL analyses measured the $^{234}\text{U}/^{238}\text{U}$, $^{235}\text{U}/^{238}\text{U}$, and $^{236}\text{U}/^{238}\text{U}$ ratios on all five spherules. Approximately 20 spot analyses were performed per spherule at LLNL and between 3 and 45 spot analyses were performed per sample at LANL (Fig. 2).

The LLNL analyses were conducted using a 5 nA, $^{16}\text{O}^-$ primary ion beam that impacted the sample with a kinetic energy of 17 keV, focused into a spot of ~10-30 μ m diameter. Positive secondary ions were accelerated to 4500 V and focused into the mass spectrometer set to a mass resolving power of ~3000, sufficient to resolve the relevant

molecular interferences, and were then counted using a single electron multiplier detector. Data were collected using two different mass sequences. Initially, data were obtained for masses 250.8 (background), 251 ($^{235}\text{U}^{16}\text{O}^+$), and 254 ($^{238}\text{U}^{16}\text{O}^+$); the intensities of $^{234}\text{U}^{16}\text{O}^+$ and $^{236}\text{U}^{16}\text{O}^+$ were below the detection limits of the instrument. In a second series of analyses, the mass table was expanded to include mass 29.8 (background) and 30 ($^{30}\text{Si}^+$) to determine the U concentration at each analysis spot by comparing the ($^{235}\text{U}^{16}\text{O}^+ + ^{238}\text{U}^{16}\text{O}^+$)/ $^{30}\text{Si}^+$ ratio to the same ratio measured in our ~350 $\mu\text{g/g}$ U-bearing glass standard.

At LLNL, a single SIMS analysis consisted of 70-100 cycles, where for each cycle, the magnetic field was adjusted to each of the analyzed masses for a user-defined period of time. A single cycle took approximately 30 seconds. Each cycle, the uranium masses were counted for 3-5 s, with typical count rates of 100-300 counts per second on $^{235}\text{U}^{16}\text{O}^+$. When we measured $^{30}\text{Si}^+$ (on spherules U3 and U4), typical count rates were 200,000-300,000 counts per second. Magnet settling times depend on the applied change in the magnetic field, but were typically on the order of ~1 s.

[Figure 2 - Backscattered electron images with SIMS analysis locations overlaid. The contrast of each image was individually adjusted to emphasize compositional zoning features and no inferences about compositional differences between the samples should be drawn from these images. Filled blue circles show the locations of the LLNL SIMS analyses (spot size: ~10-30 μm), while filled yellow squares show the locations of the LANL SIMS analyses (raster size: 25 x 25 μm). The markers have been enlarged to ease viewing and are not representative of the actual size of the SIMS analyses. Sample U1B is shown twice, as this sample was initially analyzed at LLNL, then re-polished to expose a different surface, and subsequently analyzed at LANL.]

The LANL analyses were conducted using a 20-30 nA $^{16}\text{O}^-$ primary ion beam that impacted the sample with a kinetic energy of 20 keV. Positive secondary ions were accelerated to 10 kV and detected using either mono-collection (magnetic peak switching with a single electron multiplier detector) or multi-collection (static magnetic field with multiple electron multiplier detectors). The ion transfer optics were tuned to image an 80 μm field of view using a 400 μm diameter contrast aperture and a 3000-4000 μm diameter field aperture. A mass resolving power of ~3000-4000 was used for both the mono-collector and the multi-collector analyses. Nuclear magnetic resonance control was used to stabilize the magnet for analyses performed by static multi-collection. A 40 x 40 μm area was pre-sputtered for 60 seconds, after which secondary ions were collected from a 25 x 25 μm rastered area for the sequence 233.8 (background), $^{234}\text{U}^+$, $^{235}\text{U}^+$, $^{236}\text{U}^+$, and $^{238}\text{U}^+$.

At LANL, spherules U1A, U1B, U2, and U3 were analyzed in mono-collection mode and spherule U4 was analyzed in multi-collection mode. In mono-collection, a single analysis consisted of 20-25 cycles, where cycles took approximately 30 seconds. For each cycle, the uranium masses were counted for between 2-5 s, with typical count rates of 2000-5000 counts per second on $^{235}\text{U}^+$. The magnet was settled for 1 s between masses. In multi-collection, data were collected in 2 second cycles for 50 cycles, with typical count rates of ~1700 counts per second on $^{235}\text{U}^+$.

The accuracy, precision, and instrumental mass fractionation of U isotope analyses made at LLNL and LANL were determined using two synthetic silicate glasses doped respectively with ~350 $\mu\text{g/g}$ and ~3,500 $\mu\text{g/g}$ of uranium, fabricated following the procedure outlined in Appendix A. Multi-collector inductively-coupled plasma mass spectrometry (MC-ICP-MS) was used to measure the U concentration and U-isotope composition of the glasses following procedures discussed in Appendix A; the results are shown in Table 2.

[Table 2 – U Concentrations and U isotopic ratios of our U-bearing glass standards as measured by MC-ICP-MS.]

The standards were measured periodically throughout the analytical sessions to correct for any day-to-day variability in the mass bias of the SIMS instruments. We measured the ~350 $\mu\text{g/g}$ standard 23 times at LLNL and measured the ~3,500 $\mu\text{g/g}$ standard 10 times at LANL while operating the instrument as a multi-collector and 7 times while operating as a mono-collector (Appendix A). We present the accuracy as the percent deviation of the mean of the SIMS measurements from measurements made with MC-ICP-MS (Table 2) and precision as two times the relative

standard error of the mean (Table 3). The lower precision and accuracy of the multi-collector analyses of the $^{234}\text{U}/^{238}\text{U}$ and $^{236}\text{U}/^{238}\text{U}$ ratios reflects differences in the experimental protocol, which led to poorer counting statistics for $^{234}\text{U}^+$ and $^{236}\text{U}^+$.

[Table 3 - Accuracy and precision of the SIMS measurements on our U-bearing glass standards.]

3. Results

3.1 Distribution of major elements and radionuclides

The backscattered electron images and compositional maps qualitatively show that spherules U1A and U1B are nearly circular in cross section and free of large internal variations in chemical composition (Figs. 2 and 3). The polished section of U1A contains several large (10-100s of μm) vesicles, while U1B is nearly void-free in cross-section. The regions appearing dark in the backscattered electron images and bright in the Si compositional maps of U1A and U1B consist entirely of Si and O, determined using EDS, and are likely quartz that was partially or completely melted during detonation. Sample U2 has an elongated, teardrop shape with one large vesicle and multiple smaller vesicles, and exhibits greater compositional heterogeneity than the four other samples. U3 is ~2.4 mm in maximum diameter and semi-circular in cross section with many vesicles clustered near the center, exhibiting some Ca heterogeneity and several enriched Si regions that have sharply delineated boundaries (Fig. 3). U4 is ~2.3 mm in maximum diameter and also semi-circular in cross section, with no significant voids, and like U2, appears to exhibit some large scale compositional heterogeneity, particularly with respect to Ca (Fig. 3).

[Figure 3 – Chemical compositional maps for all 5 spherules. Composition maps of Si, Al, Ca, and Fe (respectively) determined from wavelength-dispersive x-ray spectrometry mapping using EPMA. All scale bars are 500 μm .]

Nine oxides account for ~99% of the composition of the spherules (because the spherules are glassy, we assume oxides). The results of the EPMA analyses (Table 4) indicate that all five samples have similar major element chemical compositions, enriched in Si (~72% SiO_2) and Al (~14% Al_2O_3). Two samples, U2 and U4, have regions characterized by two distinct compositions, indicated by the bright and dark regions in the respective backscattered electron images and Ca compositional maps (Figs. 2 and 3). The relative standard deviation (the standard deviation divided by the mean) of the CaO concentration illustrates this difference: 7.5% for U1A versus 55% for U2 and 30% for U4. For U2, the CaO, FeO, K_2O , and MgO concentrations are significantly different ($>2\sigma$) between the bright and dark regions in the backscattered electron image and Ca compositional map (the bright region is enriched in CaO, FeO, and MgO and depleted in K_2O relative to the dark region). For U4, CaO, Al_2O_3 , and SiO_2 concentrations are significantly different between the two regions (the bright region is enriched in CaO and Al_2O_3 and depleted in SiO_2 relative to the dark region).

[Table 4 – Average major element compositions in wt.% of multiple EPMA spot analyses for all 5 spherules. The 1σ symbols refer to one standard deviation of multiple analyses.]

[Table 5 – Average major element compositions in wt.% of multiple EPMA spot analyses for different compositional regions in spherules U2 and U4. Average major element compositions in wt.% determined by EPMA for samples U2 and U4 separated into measurements made in the bright and dark regions, as determined from the backscattered electron image and Ca compositional map (Figs. 2 and 3). Measurements taken on the boundary of the regions were discarded. The 1σ symbols refer to one standard deviation of multiple analyses.]

There are large differences in radioactivity between the five samples, with U1A exhibiting much lower activity relative to U1B, which exhibits the highest activity (Fig. 4). In U1A and U1B, activity is homogeneously distributed, while U2, U3, and U4 exhibit heterogeneous activity distributions. In U2, the region of lowest activity correlates with the region of lower average atomic number (Fig. 2), that is the region relatively depleted in CaO, FeO, K_2O ,

and MgO (Fig. 3). However, U4 exhibits the opposite correlation: the region with lowest activity correlates with the region of higher average atomic number (Figs. 2), that is, the region relatively enriched in CaO and Al₂O₃ (Fig 3.).

[Figure 4 - Autoradiographs for all 5 spherules. Backscattered electron (top) and autoradiography (bottom) images of the fallout glasses characterized in this study. Backscattered electron micrographs show polished mid-sections of the samples. The contrast of each image was individually adjusted to emphasize compositional zoning features and no inferences about compositional differences between the samples should be drawn from these images. The bright region towards the center of sample U3 is sample charging. On the bottom, false color qualitative autoradiography images indicate both α and β activity (but is likely dominated by β activity due to the low specific activity of uranium in these samples), where yellow-white areas depict areas of highest activity. All five images were obtained from the same exposure and differences in color reflect relative differences in radioactivity. All scale bars are 500 μ m.]

3.2 Uranium isotope distributions

Between both analytical sessions at LLNL and LANL, we measured the $^{235}\text{U}/^{238}\text{U}$ ratio in 184 locations. Among all five spherules, the $^{235}\text{U}/^{238}\text{U}$ isotope ratio spans a factor of nearly 600, from 0.02 to 11.84 (Table 6 and Fig. 5). The lowest $^{235}\text{U}/^{238}\text{U}$ ratio ($^{235}\text{U}/^{238}\text{U}=0.02$) measured is ~ 2.75 times greater than that of natural uranium ($^{235}\text{U}/^{238}\text{U}=0.00725$). The highest $^{235}\text{U}/^{238}\text{U}$ ratio falls below that of so-called oralloy ($^{235}\text{U}/^{238}\text{U}\sim 17.3$, or $\sim 93\%$ enriched in ^{235}U), a type of highly enriched uranium common in the U.S. nuclear stockpile during the era of above ground testing (Moody, 1994). Within a single spherule, U2, the $^{235}\text{U}/^{238}\text{U}$ ratio ranges from 0.02 to 7.41, a factor of nearly 400 (Fig. 5). In MC-ICP-MS analyses of whole spherules, similar variation has been observed, but to a far lesser degree (from $^{235}\text{U}/^{238}\text{U}=2.32$ to $^{235}\text{U}/^{238}\text{U}=7.72$ in 28 samples; Eppich et al., 2014).

The 104 SIMS analyses made at LANL also measured the $^{234}\text{U}/^{238}\text{U}$ and $^{236}\text{U}/^{238}\text{U}$ ratios. These minor isotope ratios span a large range, from $^{234}\text{U}/^{238}\text{U}=0.0003$ and $^{236}\text{U}/^{238}\text{U}=0.0002$ in one analysis on spherule U2 to $^{234}\text{U}/^{238}\text{U}=0.09$ and $^{236}\text{U}/^{238}\text{U}=0.04$ in one analysis on spherule U1B (Figs. 6 and 7; Table 6). In addition, the minor U isotope ratios show a strong linear correlation among all five samples when plotted against $^{235}\text{U}/^{238}\text{U}$ (Figs. 6 and 7). For $^{234}\text{U}/^{238}\text{U}$ vs. $^{235}\text{U}/^{238}\text{U}$, a linear fit to the data has a slope and 2σ uncertainty of 0.01082 ± 0.00007 ($R^2 = 0.999$). For $^{236}\text{U}/^{238}\text{U}$ vs. $^{235}\text{U}/^{238}\text{U}$, a linear fit has a slope and 2σ uncertainty of 0.00479 ± 0.00005 ($R^2 = 0.997$). Both fits have y-intercepts that pass through the origin within 2σ uncertainty.

[Table 6 – SIMS measurements of U isotope ratios on all 5 spherules. Uncertainties are 2σ .]

Samples U1A and U1B are relatively homogeneous with respect to both chemical composition (Table 1 and Fig. 3) and uranium isotope ratios, except for the single $^{235}\text{U}/^{238}\text{U}$ ratio of 11.84 measured near the periphery of U1B (Figs. 8 and 9). The three measurements on U1A have a mean $^{235}\text{U}/^{238}\text{U}$ ratio of 3.48 and relative standard deviation of 11.0%. For U1B, the mean value of the $^{235}\text{U}/^{238}\text{U}$ ratios (excluding the 11.84 value) is 7.14, with a relative standard deviation of 8.3%. Contrast these values with the relative standard deviations on U2, U3, and U4: 76.7%, 42.7%, and 26.4%, respectively. We found no systematic variation in the $^{235}\text{U}/^{238}\text{U}$ ratio with position in these two samples and our observations suggest U1A and U1B are relatively well mixed in both major elements and uranium isotopes.

As stated above, U1B exhibits a singularly high $^{235}\text{U}/^{238}\text{U}$ ratio of 11.84 near the spherule's periphery. We explored the spatial extent of this region by translating the stage $\sim 20 \mu\text{m}$ and performing another SIMS analysis. The $^{235}\text{U}/^{238}\text{U}$ ratio in this second location is 8.16 and is indistinguishable from values elsewhere in the sample, i.e., lower by a factor of ~ 1.5 , suggesting at least this one localized U-isotope heterogeneity in U1B has a characteristic spatial scale of $\sim 10 \mu\text{m}$ or less.

U3 exhibits greater compositional (particularly with respect to Ca; Table 4 and Fig. 3) and U isotope heterogeneity compared to U1A or U1B (Fig. 10). The relative standard deviations of the Ca concentration and $^{235}\text{U}/^{238}\text{U}$ ratios for U3 are 20% and 43%, respectively (compared with U1A's respective relative standard deviations of 7.5% and 11.0%). The large relative standard deviation in the $^{235}\text{U}/^{238}\text{U}$ ratio in U3 reflects several low values near the center of the sample, which reduces to 29% if those values are excluded. There are no features in the backscattered electron

image or composition maps with which these low ratios are correlated, but the autoradiography shows a low activity region near the center of the sample (Fig. 4).

Spherules U2 and U4 exhibit correlations between U isotope ratios and major element composition (Figs. 11 and 12). In U2, two distinct U-isotope regions can be defined. One region, characterized by $1 < {}^{235}\text{U}/{}^{238}\text{U} < 8$, is enriched in CaO, FeO, and MgO (bright region in U2's Ca and Fe compositional maps), while the second region, characterized by $0.02 < {}^{235}\text{U}/{}^{238}\text{U} < 1$, is associated with the region enriched in K₂O (dark regions in U2's Ca and Fe compositional maps; Table 5, Figs. 3 and 11). The ${}^{235}\text{U}/{}^{238}\text{U}$ ratios in U4 also display a bimodal behavior. However, in contrast to U2, the regions enriched in CaO are associated with lower ${}^{235}\text{U}/{}^{238}\text{U}$ ratios (Table 5, Figs. 3 and 12). The regions enriched in CaO and Al₂O₃ (bright regions in U4's Ca compositional map) contain $2 < {}^{235}\text{U}/{}^{238}\text{U} < 4$, while the region enriched in SiO₂ and depleted in CaO and Al₂O₃ (dark regions in U4's Ca compositional map) are associated with higher ${}^{235}\text{U}/{}^{238}\text{U}$ ratios, $4 < {}^{235}\text{U}/{}^{238}\text{U} < 6.5$ (Figs. 3 and 12).

In two of the samples, U3 and U4, the ${}^{235}\text{U}/{}^{238}\text{U}$ ratio and the uranium concentration were simultaneously measured (Fig. 13 and Appendix B). The uranium concentrations range from 3 to 19 µg/g with a 2σ uncertainty of 8-15% (this uncertainty is dominated by the variability in the SiO₂ concentration in the spherules measured using EPMA), while the concentration of uranium in soil near ground zero ranges from 2.7 to 4.8 µg/g (Eppich et al., 2014). Concentrations in U3 and U4 show positive correlations with the ${}^{235}\text{U}/{}^{238}\text{U}$ ratio ($R^2=0.77$ as a combined data set with one outlier excluded; $R^2=0.68$ with the outlier included).

[Figure 5 - Histogram of all ${}^{235}\text{U}/{}^{238}\text{U}$ measurements. There are 25 bins spaced equally between ${}^{235}\text{U}/{}^{238}\text{U}=0.01$ and ${}^{235}\text{U}/{}^{238}\text{U}=20$. The preponderance of low ${}^{235}\text{U}/{}^{238}\text{U}$ ratios in U2, contrasted with higher values in U1B and U4 is apparent. Data are from LANL and LLNL.]

[Figure 6 - Composite 3-isotope plot of ${}^{234}\text{U}/{}^{238}\text{U}$ vs. ${}^{235}\text{U}/{}^{238}\text{U}$ for all spherules. Uncertainties are 2σ. Data are from LANL.]

[Figure 7 Composite 3-isotope plot of ${}^{236}\text{U}/{}^{238}\text{U}$ vs. ${}^{235}\text{U}/{}^{238}\text{U}$ for all spherules. Uncertainties are 2σ. Data are from LANL.]

[Figure 8 - ${}^{235}\text{U}/{}^{238}\text{U}$ vs. distance from the spherule's center on U1A. Uncertainties are 2σ. Data are from LANL.]

[Figure 9 - ${}^{235}\text{U}/{}^{238}\text{U}$ vs. distance from the spherule's center on U1B. Note the singularly high ${}^{235}\text{U}/{}^{238}\text{U}$ ratio of 11.84 near the periphery. Uncertainties are 2σ. Data are from LANL and LLNL.]

[Figure 10 - ${}^{235}\text{U}/{}^{238}\text{U}$ vs. distance from the spherule's center on U3. Uncertainties are 2σ. Data are from LANL and LLNL.]

[Figure 11 - ${}^{235}\text{U}/{}^{238}\text{U}$ vs. distance from the spherule's center on U2. Note the logarithmic ordinate scale. Data are separated into SIMS measurements taken in the bright and dark regions, as defined in the text and shown in the backscattered electron image and Ca and Fe compositional maps (Figs. 2 and 3). Uncertainties are 2σ. Data are from LANL and LLNL.]

[Figure 12 - ${}^{235}\text{U}/{}^{238}\text{U}$ vs. distance from the spherule's center on U4. Data are separated into SIMS measurements taken in the bright and dark regions, as defined in the text and shown in the backscattered electron image and Ca compositional map (Figs. 2 and 3). Uncertainties are 2σ. Data are from LANL and LLNL.]

[Figure 13 - ${}^{235}\text{U}/{}^{238}\text{U}$ vs. uranium concentration for samples U3 and U4. The vertical bar represents the range of U concentrations measured in five soil samples proximate to ground zero (between 2.7 and 4.8 µg/g; Eppich et al., 2014). Uncertainties are 2σ. Data are from LLNL.]

4. Discussion

4.1 Comparisons to ground glass

Our results show differences between ground glass and aerodynamic glassy fallout. Both types of fallout are known to be heterogeneous mixtures with respect to major elements, likely due to natural heterogeneities in the local geology and rapid heating and quenching (Fahey et al., 2010; Eby et al., 2010; Sharp et al., 2014). However, with respect to a direct device component such as unfissioned fuel, ground glass appears to be extremely heterogeneous (Fahey et al., 2010), while this study shows that the degree of heterogeneity varies greatly from sample to sample in aerodynamic glassy fallout. In one spherule, U2, the U isotopic ratio varies by nearly a factor of 400, and in another spherule, U1B, if the outlier of 11.84 is excluded, the U isotopic ratio varies by less than 10%.

Further distinguishing ground glass and aerodynamic glassy fallout, the compositional and U isotopic variation observed in U2 and U4 suggests this spherule formed through the collision and mixing of two or more relatively large, molten objects of dissimilar composition. As can be seen in the compositional maps, two primary compositional regions can be defined in each U2 and U4 (Figs. 2 and 3). Each of those regions are also distinct with respect to U isotopes, which implies that the melts from these two regions must have mixed with different amounts of U from the device before agglomerating. The final agglomerated objects experienced little mixing before fusing. However, this study cannot determine the extent to which each of those regions were themselves formed by molten agglomeration.

Another distinguishing feature of this type of fallout is how homogenous U isotopes and major elements may appear in individual spherules. U1A and U1B are nearly homogeneous with respect to U isotopes and major elements, so they may have been held above the melting temperature (~1300 K, determined by MELTS calculations of liquidus temperatures for glasses of these compositions; Ghiorso and Sack, 1995; Asimow and Ghiorso, 1998) long enough or experienced a high enough temperature for the combined effects of convection and diffusion to effectively homogenize the silicate melts. Alternatively, they may have formed by a parcel or parcels of melt that were initially homogenous with respect to composition and U isotopic composition.

4.2 Mixing between natural and enriched uranium

The observed range of U isotope ratios in the spherules provide evidence for mixing between at least two sources of uranium with different isotopic compositions. As stated above, the maximum observed $^{235}\text{U}/^{238}\text{U}$ ratio in this study, 11.84 (~91.5% enriched in ^{235}U , assuming 1% ^{234}U) approaches the $^{235}\text{U}/^{238}\text{U}$ ratio in or alloy ($^{235}\text{U}/^{238}\text{U} \sim 17.3$), while the minimum measured $^{235}\text{U}/^{238}\text{U}$ ratio, ~0.02 in sample U2, approaches the $^{235}\text{U}/^{238}\text{U}$ value found in natural uranium, $^{235}\text{U}/^{238}\text{U} = 0.00725$. Here we calculate the relative contribution to each $^{235}\text{U}/^{238}\text{U}$ isotopic ratio measurement by natural uranium and or alloy, assuming that these are the only two mixing end-members. The correlated variations in the minor isotope ratios, $^{234}\text{U}/^{238}\text{U}$ and $^{236}\text{U}/^{238}\text{U}$, are also consistent with mixing between these two end-members.

This calculation assumes (1) the only source of enriched uranium can be represented by or alloy from the device and (2) isotopic fractionation of uranium in the silicate melt can be neglected.

To a good approximation, we may ignore the minor isotopes in natural uranium given that ^{234}U only ~0.0055% and the ^{236}U content in natural uranium is vanishingly small (Richter et al., 1999). With these assumptions, let the isotopic abundances of ^{235}U and ^{238}U in natural uranium be represented as $y_{235} = 0.00725$ and $y_{238} = 0.99275$. Similarly, let x_{235} and x_{238} represent the abundances of ^{235}U and ^{238}U in the enriched uranium end-member. Let n_f and n_n represent, respectively, the contributions from the enriched and natural uranium end-members in an individual SIMS measurement. The number of atoms of ^{235}U and ^{238}U in an individual measurement is given by:

$$^{235}\text{U}: n_{235} = n_f x_{235} + n_n y_{235}, \quad (1a)$$

$$^{238}\text{U}: n_{238} = n_f x_{238} + n_n y_{238}. \quad (1b)$$

The $^{235}\text{U}/^{238}\text{U}$ ratio may then be represented as:

$$\frac{n_{235}}{n_{238}} = \frac{n_f x_{235} + n_n y_{235}}{n_f x_{238} + n_n y_{238}}. \quad (2)$$

Solving Equation 2 for n_n/n_f gives an expression of the relative contribution from the two uranium isotope end-members to each U isotope ratio:

$$\frac{n_n}{n_f} = \frac{x_{235} - \frac{n_{235}}{n_{238}}x_{238}}{\frac{n_{235}}{n_{238}}y_{238} - y_{235}}. \quad (3)$$

Equation 3 plotted using our measurements is shown in Figure 14, which illustrates the range of mixing between the assumed uranium isotope end-members observed in this study.

[Figure 14 - Ratio of natural to enriched U for each SIMS analysis. Contributions of uranium of natural isotopic composition (n_n) relative to uranium from the enriched (HEU) end-member (n_f) as a function of the $^{235}\text{U}/^{238}\text{U}$ ratio for samples U1A, U1B, U2, U3, and U4, calculated from Equation 3. The dashed line represents the solution to Equation 3 and depicts the shape of the mixing line. The mixing line asymptotically approaches infinity as the $^{235}\text{U}/^{238}\text{U}$ ratio approaches the composition of natural uranium, $^{235}\text{U}/^{238}\text{U} = 0.00725$, and asymptotically approaches zero as the $^{235}\text{U}/^{238}\text{U}$ ratio approaches 17.3, the $^{235}\text{U}/^{238}\text{U}$ ratio in or alloy (Moody, 1994). If the uncertainties (2σ) are not visible, they are smaller than the points.]

5. Conclusions

Five fallout spherules were characterized using SIMS, SEM/EDS, EPMA, and autoradiography. Individual spherules display distinct compositional heterogeneity suggestive of rapid cooling and incomplete mixing, exhibiting heterogeneity in U isotopes with $0.02 < ^{235}\text{U}/^{238}\text{U} < 11.84$ among the five spherules and $0.02 < ^{235}\text{U}/^{238}\text{U} < 7.84$ within a single spherule. The large heterogeneity in the uranium isotope ratios confirms that these spherules preserve a mixture of uranium from at least two end-members with distinct uranium isotope compositions. The extent of mixing and the magnitude of uranium isotopic heterogeneity provide important constraints on the thermal history of aerodynamic fallout glasses, and point the way to developing a more quantitative understanding of the formation of fallout.

Two samples (U1A and U1B) are far more relatively homogenous with respect to both major element composition and uranium isotopes than the other three (U2, U3, and U4), suggesting these objects had longer residence times within the fireball at high temperature or were formed from approximately homogenous precursors, with respect to composition and uranium isotopes. The $^{235}\text{U}/^{238}\text{U}$ ratio is correlated with major element composition in two spherules, suggesting agglomeration of molten or partially molten precursors, followed by rapid cooling. Correlated variations among the $^{234}\text{U}/^{238}\text{U}$, $^{235}\text{U}/^{238}\text{U}$, and $^{236}\text{U}/^{238}\text{U}$ ratios point to mixing between end-member components corresponding to highly enriched uranium derived from the device and natural uranium. We use a two-component mixing model, one end-member being natural uranium and the other having the composition of or alloy (HEU), to illustrate the range of mixing between natural and enriched U in these fallout glasses.

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Appendix A - Fabrication and measurements of U-bearing standard glasses

A.1 Fabrication of the U-bearing standard glasses

The standard glasses were prepared by doping a base glass composition corresponding to one of the eutectic compositions in the CaO-Al₂O₃-SiO₂ system. The nominal composition is SiO₂=62 wt.%, Al₂O₃=14.5 wt.% and CaO= 23.5 wt.%. This composition has a melting temperature of 1170°C. The base glass composition was prepared from reagent grade SiO₂, Al₂O₃, and CaCO₃. The oxide-carbonate mix was ground under ethanol in an automated agate mortar and pestle for 60 minutes and then dried under a heat lamp. The mix was then calcined in a platinum crucible in air at 850°C overnight to decompose the CaCO₃. The calcine was then ground under ethanol in an automated agate mortar and pestle for 60 minutes and then dried under a heat lamp. Finally, the base glass calcine was fused in a bottom-loading Deltech furnace in a platinum crucible for a minimum of 8 hours at 1450°C and quenched in water, producing a clear glass. The glass was then crushed in a hardened steel mortar and pestle, and then ground under ethanol in an automated agate mortar and pestle for 60 minutes. This fusion-grinding procedure was repeated two additional times.

The U-doped glasses were prepared by adding nitrate solutions containing 10,000 ppm of certified reference material (CRM) U500 to the base glass to obtain glasses with uranium concentrations of ~500 and ~5,000 µg/g. The solution was pipetted into ~5 g of the base glass for each of the glasses. Next, the mixture was ground by hand in a fume hood under ethanol in an agate mortar and pestle for 60 minutes and dried.

Each mixture was fused in a bottom-loading Deltech furnace in a new platinum crucible for a minimum of 8 hours at 1450°C and quenched in water. A separate crucible was used for each concentration to minimize cross-contamination. Following each fusion step, the glass was removed from the crucible and coarsely ground in a hardened steel mortar. The coarse mix was then ground under ethanol in an agate mortar and pestle for 60 minutes and dried. The fusion/grinding cycle was repeated a minimum of three times for each sample.

A.2 Isotopic and concentration measurements of the U-bearing standard glasses via MC-ICP-MS

The standard glasses were measured for U isotope ratios and U concentrations using a Nu Plasma I high resolution MC-ICP-MS instrument. We used the U010 certified reference material for instrumental mass bias corrections. Each glass was once for U isotopics and once, on a separately prepared aliquot using isotope dilution (spiked with ²³³U), to obtain U concentrations.

The MC-ICP-MS measurements show that the glasses deviate from the desired concentrations of ~500 and ~5,000 µg/g of U and from the certified U isotope ratios of CRM U500 (Tables 2 and A1). The deviation of the U isotope ratios in the U-bearing standard glasses from the CRM U500 dopant is likely due to U contamination during the fabrication process.

[Table A1: Deviations of U isotope ratios in LLNL and LANL standard glasses from CRM U500. Uncertainties are 2σ.]

A.3 SIMS measurements of the U-bearing standard glasses

[Table A2: LLNL SIMS measurements of ²³⁵U/²³⁸U on the ~350 µg/g U-bearing glass standard. Uncertainties are 2σ.]

[Table A3: LANL SIMS measurements of ²³⁴U/²³⁸U, ²³⁵U/²³⁸U, and ²³⁶U/²³⁸U on the ~3,500 µg/g U-bearing glass standard. Modes refer to whether the instrument was operating as a mono-collector or multi-collector. Uncertainties are 2σ.]

Appendix B - U concentration data for spherules U3 and U4

[Table B1: LLNL SIMS measurements of the U concentration and their corresponding ²³⁵U/²³⁸U ratios for spherules U3 and U4. The first measurement on spherule U3 was excluded because the composition of the analyzed region was highly enriched in Ca and highly depleted in Si, invalidating the use of the (²³⁵U¹⁶O⁺ + ²³⁸U¹⁶O⁺)/³⁰Si⁺ ratio as a method to estimate the U concentration in that location. Uncertainties are 2σ.]

559 Table 1

Sample	Mass (mg)	Avg. Diameter (mm)
U1A	3.7	1.6
U1B	2.5	1.4
U2	4.5	1.6
U3	14.8	2.3
U4	14.4	2.2

560 Table 2

Standard	U Concentration ($\mu\text{g/g}$)			2σ	$^{235}\text{U}/^{238}\text{U}$			2σ	$^{234}\text{U}/^{238}\text{U}$			2σ	$^{236}\text{U}/^{238}\text{U}$			2σ
LLNL	359.1	$\pm$	1.2		0.9618	$\pm$	0.0013		0.010044	$\pm$	0.000006		0.001479	$\pm$	0.000006	
LANL	3490	$\pm$	12		0.9949	$\pm$	0.0014		0.010371	$\pm$	0.000006		0.001521	$\pm$	0.000005	

561 Table 3

Standard	Mode	# analyses	$^{235}\text{U}/^{238}\text{U}$		$^{234}\text{U}/^{238}\text{U}$		$^{236}\text{U}/^{238}\text{U}$	
			Accuracy (%)	Precision (%)	Accuracy (%)	Precision (%)	Accuracy (%)	Precision (%)
LLNL	mono	23	0.40	0.30	-	-	-	-
LANL	mono	7	1.06	0.17	1.62	0.22	1.03	0.49
LANL	multi	10	0.67	0.05	0.35	0.36	0.02	1.06

52 Table 4
53

Sample	# pts	SiO ₂		1σ	Al ₂ O ₃		1σ	CaO		1σ	K ₂ O		1σ	Na ₂ O		1σ	FeO		1σ	TiO ₂		1σ	MnO		1σ	MgO		1σ	Sum
U1A	39	72.36	±	1.35	14.56	±	0.81	1.41	±	0.18	3.69	±	0.12	3.11	±	0.15	3.67	±	0.22	0.33	±	0.02	0.13	±	0.02	0.60	±	0.06	99.86
U1B	49	71.75	±	0.74	14.49	±	0.52	1.84	±	0.14	3.64	±	0.11	3.12	±	0.10	3.44	±	0.21	0.28	±	0.03	0.09	±	0.02	0.58	±	0.04	99.23
U2	48	72.18	±	1.99	13.49	±	1.25	1.10	±	0.61	4.94	±	0.53	3.72	±	0.41	2.27	±	0.83	0.23	±	0.06	0.11	±	0.03	0.38	±	0.20	98.42
U3	44	71.43	±	1.67	13.65	±	1.02	2.55	±	0.51	3.87	±	0.21	3.36	±	0.22	3.27	±	0.21	0.29	±	0.03	0.15	±	0.02	0.64	±	0.06	99.21
U4	49	71.90	±	4.08	14.30	±	2.27	2.61	±	0.76	3.54	±	0.54	2.97	±	0.46	3.22	±	0.50	0.29	±	0.05	0.13	±	0.03	0.56	±	0.10	99.52

564
565 Table 5
566

Sample	# pts	SiO ₂		1σ	Al ₂ O ₃		1σ	CaO		1σ	K ₂ O		1σ	FeO		1σ	MgO		1σ
U2 (bright)	14	70.93	±	1.38	13.34	±	1.20	1.79	±	0.19	4.44	±	0.21	3.20	±	0.27	0.59	±	0.07
U2 (dark)	13	72.83	±	0.92	14.06	±	0.61	0.45	±	0.24	5.50	±	0.29	1.36	±	0.22	0.16	±	0.07
U4 (bright)	13	69.59	±	0.59	15.54	±	0.40	3.37	±	0.14	3.44	±	0.06	3.18	±	0.10	0.58	±	0.02
U4 (dark)	17	72.51	±	1.02	13.96	±	0.56	2.14	±	0.39	3.71	±	0.28	3.37	±	0.26	0.58	±	0.06

57 Table 6

U1A	²³⁵ U/ ²³⁸ U	2σ	²³⁴ U/ ²³⁸ U	2σ	²³⁶ U/ ²³⁸ U	2σ	U2	²³⁵ U/ ²³⁸ U	2σ	²³⁴ U/ ²³⁸ U	2σ	²³⁶ U/ ²³⁸ U	2σ	U2 (cont.)	²³⁵ U/ ²³⁸ U	2σ	²³⁴ U/ ²³⁸ U	2σ	²³⁶ U/ ²³⁸ U	2σ
LANL-1	3.850 ± 0.064		0.0416 ± 0.0018		0.01822 ± 0.00111		LANL-1	3.372 ± 0.043		0.0360 ± 0.0016		0.01751 ± 0.00095		LANL-36	5.133 ± 0.043		0.0553 ± 0.0012		0.02482 ± 0.00082	
LANL-2	3.084 ± 0.051		0.0329 ± 0.0017		0.01538 ± 0.00110		LANL-2	3.841 ± 0.055		0.0416 ± 0.0014		0.01971 ± 0.00092		LANL-37	1.039 ± 0.026		0.0110 ± 0.0004		0.00483 ± 0.00034	
LANL-3	3.519 ± 0.074		0.0384 ± 0.0029		0.01886 ± 0.00151		LANL-3	2.178 ± 0.076		0.0239 ± 0.0011		0.01127 ± 0.00061		LANL-38	2.340 ± 0.023		0.0256 ± 0.0007		0.01114 ± 0.00044	
U1B	²³⁵ U/ ²³⁸ U	2σ	²³⁴ U/ ²³⁸ U	2σ	²³⁶ U/ ²³⁸ U	2σ	LANL-4	1.220 ± 0.011		0.0131 ± 0.0005		0.00615 ± 0.00033		LANL-39	2.390 ± 0.038		0.0253 ± 0.0008		0.01172 ± 0.00050	
LANL - 1	7.609 ± 0.103		0.0836 ± 0.0025		0.03564 ± 0.00171		LANL-5	3.187 ± 0.029		0.0346 ± 0.0009		0.01644 ± 0.00068		LANL-40	4.474 ± 0.046		0.0476 ± 0.0010		0.02154 ± 0.00067	
LANL - 2	7.339 ± 0.092		0.0795 ± 0.0023		0.03476 ± 0.00141		LANL-6	3.086 ± 0.025		0.0336 ± 0.0008		0.01557 ± 0.00056		LANL-41	5.132 ± 0.039		0.0546 ± 0.0011		0.02393 ± 0.00069	
LANL - 3	6.142 ± 0.081		0.0674 ± 0.0021		0.02997 ± 0.00131		LANL-7	1.576 ± 0.019		0.0174 ± 0.0006		0.00795 ± 0.00041		LANL-42	5.225 ± 0.040		0.0566 ± 0.0013		0.02497 ± 0.00076	
LANL - 4	7.172 ± 0.091		0.0767 ± 0.0025		0.03441 ± 0.00141		LANL-8	2.595 ± 0.085		0.0282 ± 0.0012		0.01309 ± 0.00046		LANL-43	4.962 ± 0.036		0.0532 ± 0.0010		0.02350 ± 0.00063	
LANL - 5	7.264 ± 0.093		0.0785 ± 0.0023		0.03566 ± 0.00151		LANL-9	2.953 ± 0.035		0.0318 ± 0.0008		0.01502 ± 0.00053		LANL-44	5.972 ± 0.061		0.0647 ± 0.0016		0.02883 ± 0.00111	
LANL - 6	8.637 ± 0.120		0.0940 ± 0.0029		0.04198 ± 0.00172		LANL-10	0.607 ± 0.011		0.0071 ± 0.0003		0.00311 ± 0.00026		LANL-45	5.420 ± 0.054		0.0586 ± 0.0015		0.02608 ± 0.00112	
LANL - 7	7.121 ± 0.098		0.0760 ± 0.0023		0.03554 ± 0.00151		LANL-11	0.838 ± 0.031		0.0095 ± 0.0005		0.00439 ± 0.00027		LLNL-1	7.408 ± 0.236					
LANL - 8	6.284 ± 0.090		0.0664 ± 0.0028		0.03003 ± 0.00141		LANL-12	2.341 ± 0.043		0.0256 ± 0.0008		0.01187 ± 0.00056		LLNL-2	3.763 ± 0.154					
LANL - 9	7.052 ± 0.244		0.0792 ± 0.0063		0.03261 ± 0.00321		LANL-13	5.716 ± 0.055		0.0625 ± 0.0012		0.02798 ± 0.00080		LLNL-3	2.853 ± 0.100					
LANL - 10	7.248 ± 0.097		0.0776 ± 0.0029		0.03512 ± 0.00161		LANL-14	2.631 ± 0.029		0.0289 ± 0.0009		0.01300 ± 0.00070		LLNL-4	2.827 ± 0.121					
LANL - 11	7.451 ± 0.099		0.0799 ± 0.0027		0.03585 ± 0.00151		LANL-15	4.599 ± 0.043		0.0488 ± 0.0011		0.02227 ± 0.00070		LLNL-5	4.130 ± 0.177					
LANL - 12	6.085 ± 0.106		0.0649 ± 0.0027		0.02910 ± 0.00151		LANL - 16	5.006 ± 0.049		0.0544 ± 0.0013		0.02456 ± 0.00074		LLNL-6	1.475 ± 0.090					
LLNL - 1	6.576 ± 0.129						LANL - 17	4.295 ± 0.042		0.0468 ± 0.0012		0.02106 ± 0.00077		LLNL-7	0.113 ± 0.005					
LLNL - 2	7.215 ± 0.151						LANL - 18	0.044 ± 0.003		0.0005 ± 0.0001		0.00021 ± 0.00009		LLNL-8	4.713 ± 0.138					
LLNL - 3	7.185 ± 0.166						LANL - 19	2.767 ± 0.026		0.0297 ± 0.0007		0.01326 ± 0.00043		LLNL-9	3.744 ± 0.153					
LLNL - 4	7.967 ± 0.119						LANL - 20	0.076 ± 0.002		0.0008 ± 0.0002		0.00038 ± 0.00010		LLNL-10	2.119 ± 0.060					
LLNL - 5	7.421 ± 0.134						LANL - 21	0.110 ± 0.002		0.0013 ± 0.0001		0.00056 ± 0.00009		LLNL-11	4.687 ± 0.182					
LLNL - 6	7.326 ± 0.110						LANL - 22	0.165 ± 0.004		0.0017 ± 0.0002		0.00080 ± 0.00013		LLNL-12	5.013 ± 0.140					
LLNL - 7	7.081 ± 0.095						LANL - 23	1.232 ± 0.011		0.0129 ± 0.0005		0.00624 ± 0.00035		LLNL-13	2.711 ± 0.129					
LLNL - 8	7.718 ± 0.107						LANL - 24	3.887 ± 0.039		0.0427 ± 0.0012		0.01932 ± 0.00076		LLNL-14	0.022 ± 0.002					
LLNL - 9	8.025 ± 0.104						LANL - 25	0.745 ± 0.010		0.0078 ± 0.0004		0.00361 ± 0.00027		LLNL-15	2.816 ± 0.104					
LLNL - 10	6.676 ± 0.083						LANL - 26	1.164 ± 0.019		0.0126 ± 0.0006		0.00547 ± 0.00038		LLNL-16	0.202 ± 0.006					
LLNL - 11	6.768 ± 0.098						LANL - 27	4.447 ± 0.037		0.0479 ± 0.0011		0.02115 ± 0.00082		LLNL-17	1.010 ± 0.045					
LLNL - 12	6.867 ± 0.091						LANL - 28	3.008 ± 0.024		0.0328 ± 0.0008		0.01457 ± 0.00066		LLNL-18	0.234 ± 0.022					
LLNL - 13	6.354 ± 0.049						LANL - 29	3.344 ± 0.027		0.0360 ± 0.0009		0.01650 ± 0.00057		LLNL-19	0.315 ± 0.031					
LLNL - 14	7.070 ± 0.127						LANL - 30	0.192 ± 0.003		0.0020 ± 0.0002		0.00098 ± 0.00013		LLNL-20	0.350 ± 0.029					
LLNL - 15	6.772 ± 0.152						LANL - 31	0.301 ± 0.005		0.0033 ± 0.0003		0.00158 ± 0.00016								
LLNL - 16	6.575 ± 0.119						LANL - 32	0.052 ± 0.002		0.0005 ± 0.0001		0.00022 ± 0.00008								
LLNL - 17	7.059 ± 0.146						LANL - 33	0.034 ± 0.002		0.0003 ± 0.0001		0.00017 ± 0.00005								
LLNL - 18	11.843 ± 0.219						LANL - 34	0.126 ± 0.002		0.0013 ± 0.0001		0.00061 ± 0.00007								
LLNL - 19	8.162 ± 0.133						LANL - 35	0.288 ± 0.004		0.0029 ± 0.0002		0.00146 ± 0.00014								

U3	$^{235}\text{U}/^{238}\text{U}$	2σ	$^{234}\text{U}/^{238}\text{U}$	2σ	$^{236}\text{U}/^{238}\text{U}$	2σ	U3 (cont.)	$^{235}\text{U}/^{238}\text{U}$	2σ	$^{234}\text{U}/^{238}\text{U}$	2σ	$^{236}\text{U}/^{238}\text{U}$	2σ
LANL - 1	3.236 ± 0.076		0.0343 ± 0.0023		0.01582 ± 0.00149		LLNL - 16	0.413 ± 0.026					
LANL - 2	2.180 ± 0.034		0.0242 ± 0.0012		0.01097 ± 0.00082		LLNL - 17	1.154 ± 0.033					
LANL - 3	3.118 ± 0.039		0.0337 ± 0.0012		0.01443 ± 0.00081		LLNL - 18	0.241 ± 0.010					
LANL - 4	3.768 ± 0.047		0.0403 ± 0.0013		0.01766 ± 0.00093		LLNL - 19	0.899 ± 0.056					
LANL - 5	3.838 ± 0.043		0.0423 ± 0.0014		0.01807 ± 0.00098		LLNL - 20	2.627 ± 0.079					
LANL - 6	3.898 ± 0.048		0.0425 ± 0.0015		0.01957 ± 0.00086		LLNL - 21	3.042 ± 0.078					
LANL - 7	3.662 ± 0.029		0.0401 ± 0.0009		0.01783 ± 0.00062		LLNL - 22	4.324 ± 0.143					
U4	$^{235}\text{U}/^{238}\text{U}$	2σ	$^{234}\text{U}/^{238}\text{U}$	2σ	$^{236}\text{U}/^{238}\text{U}$	2σ	U4	$^{235}\text{U}/^{238}\text{U}$	2σ	$^{234}\text{U}/^{238}\text{U}$	2σ	$^{236}\text{U}/^{238}\text{U}$	2σ
LANL - 9	2.047 ± 0.020		0.0221 ± 0.0007		0.01003 ± 0.00046		LANL - 1	4.708 ± 0.070		0.0491 ± 0.0028		0.02298 ± 0.00159	
LANL - 10	2.923 ± 0.026		0.0316 ± 0.0008		0.01412 ± 0.00053		LANL - 2	4.596 ± 0.066		0.0523 ± 0.0024		0.02369 ± 0.00164	
LANL - 11	4.030 ± 0.040		0.0430 ± 0.0010		0.01971 ± 0.00070		LANL - 3	4.635 ± 0.063		0.0496 ± 0.0026		0.02346 ± 0.00161	
LANL - 12	3.779 ± 0.038		0.0399 ± 0.0012		0.01795 ± 0.00076		LANL - 4	3.935 ± 0.067		0.0430 ± 0.0024		0.02165 ± 0.00161	
LANL - 13	4.585 ± 0.045		0.0495 ± 0.0013		0.02307 ± 0.00086		LANL - 5	3.811 ± 0.061		0.0416 ± 0.0022		0.01800 ± 0.00136	
LANL - 14	5.712 ± 0.073		0.0613 ± 0.0021		0.02850 ± 0.00123		LANL - 6	3.075 ± 0.038		0.0332 ± 0.0017		0.01539 ± 0.00121	
LANL - 15	4.713 ± 0.064		0.0501 ± 0.0016		0.02293 ± 0.00103		LANL - 7	3.218 ± 0.034		0.0344 ± 0.0018		0.01570 ± 0.00116	
LANL - 16	3.834 ± 0.042		0.0413 ± 0.0016		0.01855 ± 0.00084		LANL - 8	3.953 ± 0.049		0.0443 ± 0.0022		0.01979 ± 0.00150	
LANL - 17	2.517 ± 0.029		0.0271 ± 0.0009		0.01267 ± 0.00063		LANL - 9	4.204 ± 0.052		0.0461 ± 0.0022		0.02045 ± 0.00146	
LANL - 18	3.208 ± 0.033		0.0344 ± 0.0011		0.01534 ± 0.00071		LANL - 10	3.869 ± 0.047		0.0423 ± 0.0024		0.01970 ± 0.00149	
LANL - 19	4.629 ± 0.046		0.0506 ± 0.0015		0.02311 ± 0.00087		LANL - 11	5.225 ± 0.066		0.0565 ± 0.0026		0.02547 ± 0.00175	
LANL - 20	4.520 ± 0.052		0.0483 ± 0.0014		0.02231 ± 0.00088		LANL - 12	4.737 ± 0.068		0.0491 ± 0.0024		0.02342 ± 0.00165	
LANL - 21	1.103 ± 0.019		0.0118 ± 0.0006		0.00536 ± 0.00041		LANL - 13	5.237 ± 0.064		0.0588 ± 0.0028		0.02433 ± 0.00177	
LANL - 22	0.522 ± 0.008		0.0055 ± 0.0004		0.00248 ± 0.00027		LANL - 14	5.150 ± 0.066		0.0565 ± 0.0030		0.02551 ± 0.00185	
LANL - 23	4.121 ± 0.042		0.0442 ± 0.0013		0.02018 ± 0.00093		LANL - 15	5.164 ± 0.070		0.0557 ± 0.0033		0.02430 ± 0.00196	
LANL - 24	4.034 ± 0.039		0.0434 ± 0.0013		0.01959 ± 0.00075		LANL - 16	5.344 ± 0.069		0.0593 ± 0.0032		0.02682 ± 0.00198	
LANL - 25	5.317 ± 0.054		0.0576 ± 0.0015		0.02605 ± 0.00088		LLNL - 1	5.890 ± 0.135					
LANL - 26	6.565 ± 0.058		0.0708 ± 0.0014		0.03211 ± 0.00099		LLNL - 2	6.246 ± 0.115					
LANL - 27	4.414 ± 0.053		0.0477 ± 0.0013		0.02176 ± 0.00088		LLNL - 3	5.707 ± 0.111					
LANL - 28	5.152 ± 0.053		0.0572 ± 0.0014		0.02466 ± 0.00086		LLNL - 4	6.092 ± 0.114					
LLNL - 1	5.454 ± 0.115						LLNL - 5	1.904 ± 0.053					
LLNL - 2	4.394 ± 0.125						LLNL - 6	3.924 ± 0.076					
LLNL - 3	5.478 ± 0.114						LLNL - 7	2.956 ± 0.055					
LLNL - 4	4.282 ± 0.101						LLNL - 8	2.938 ± 0.061					
LLNL - 5	3.971 ± 0.106						LLNL - 9	4.317 ± 0.115					
LLNL - 6	1.911 ± 0.079						LLNL - 10	5.102 ± 0.124					
LLNL - 7	3.158 ± 0.088						LLNL - 11	5.435 ± 0.123					
LLNL - 8	4.092 ± 0.096						LLNL - 12	5.859 ± 0.130					
LLNL - 9	4.326 ± 0.100						LLNL - 13	5.162 ± 0.144					
LLNL - 10	6.779 ± 0.178						LLNL - 14	4.669 ± 0.101					
LLNL - 11	4.901 ± 0.108						LLNL - 15	3.047 ± 0.080					
LLNL - 12	4.469 ± 0.110						LLNL - 16	5.847 ± 0.148					
LLNL - 13	6.114 ± 0.191						LLNL - 17	2.462 ± 0.070					
LLNL - 14	4.476 ± 0.119						LLNL - 18	3.314 ± 0.075					
LLNL - 15	3.076 ± 0.058						LLNL - 19	2.113 ± 0.049					

Standard	$^{235}\text{U}/^{238}\text{U}$			$^{234}\text{U}/^{238}\text{U}$			$^{236}\text{U}/^{238}\text{U}$		
		$\pm$	2σ		$\pm$			$\pm$	2σ
CRM U500 Certificate	0.9997	$\pm$	0.0014	0.010422	$\pm$	0.000019	0.001519	$\pm$	0.000006
LLNL (350 $\mu\text{g/g U}$)	0.9618	$\pm$	0.0013	0.010044	$\pm$	0.000006	0.001479	$\pm$	0.000006
Deviation (%)	-3.79	$\pm$	0.19	-3.63	$\pm$	0.19	-2.62	$\pm$	0.57
LANL (3,500 $\mu\text{g/g U}$)	0.9949	$\pm$	0.0014	0.010371	$\pm$	0.000006	0.001521	$\pm$	0.000005
Deviation (%)	-0.48	$\pm$	0.20	-0.49	$\pm$	0.19	0.15	$\pm$	0.53

Analysis #	$^{235}\text{U}/^{238}\text{U}$		2σ
1	0.974	$\pm$	0.014
2	0.955	$\pm$	0.011
3	0.965	$\pm$	0.008
4	0.961	$\pm$	0.010
5	0.967	$\pm$	0.008
6	0.955	$\pm$	0.009
7	0.968	$\pm$	0.011
8	0.960	$\pm$	0.014
9	0.975	$\pm$	0.009
10	0.970	$\pm$	0.012
11	0.968	$\pm$	0.010
12	0.970	$\pm$	0.012
13	0.968	$\pm$	0.007
14	0.969	$\pm$	0.014
15	0.971	$\pm$	0.017
16	0.959	$\pm$	0.014
17	0.974	$\pm$	0.014
18	0.965	$\pm$	0.019
19	0.957	$\pm$	0.011
20	0.956	$\pm$	0.023
21	0.979	$\pm$	0.012
22	0.969	$\pm$	0.007
23	0.955	$\pm$	0.010

Analysis #	Mode	$^{235}\text{U}/^{238}\text{U}$			$^{234}\text{U}/^{238}\text{U}$			$^{236}\text{U}/^{238}\text{U}$		
			$\pm$	2σ		$\pm$	2σ		$\pm$	2σ
1	mono	1.0042	$\pm$	0.0018	0.01059	$\pm$	0.00005	0.00152	$\pm$	0.00002
2	mono	1.0057	$\pm$	0.0018	0.01051	$\pm$	0.00006	0.00153	$\pm$	0.00002
3	mono	1.0074	$\pm$	0.0041	0.01052	$\pm$	0.00007	0.00154	$\pm$	0.00002
4	mono	1.0084	$\pm$	0.0055	0.01057	$\pm$	0.00008	0.00154	$\pm$	0.00002
5	mono	1.0018	$\pm$	0.0043	0.01050	$\pm$	0.00008	0.00153	$\pm$	0.00003
6	mono	1.0066	$\pm$	0.0059	0.01054	$\pm$	0.00010	0.00155	$\pm$	0.00002
7	mono	1.0040	$\pm$	0.0010	0.01053	$\pm$	0.00005	0.00154	$\pm$	0.00002
8	multi	1.0022	$\pm$	0.0016	0.01044	$\pm$	0.00011	0.00154	$\pm$	0.00004
9	multi	1.0011	$\pm$	0.0016	0.01047	$\pm$	0.00012	0.00152	$\pm$	0.00005
10	multi	1.0024	$\pm$	0.0021	0.01037	$\pm$	0.00014	0.00154	$\pm$	0.00004
11	multi	1.0004	$\pm$	0.0019	0.01047	$\pm$	0.00012	0.00151	$\pm$	0.00005
12	multi	1.0011	$\pm$	0.0017	0.01039	$\pm$	0.00014	0.00152	$\pm$	0.00005
13	multi	1.0013	$\pm$	0.0017	0.01032	$\pm$	0.00012	0.00155	$\pm$	0.00005
14	multi	1.0020	$\pm$	0.0018	0.01044	$\pm$	0.00012	0.00151	$\pm$	0.00005
15	multi	1.0011	$\pm$	0.0021	0.01032	$\pm$	0.00012	0.00156	$\pm$	0.00005
16	multi	1.0009	$\pm$	0.0017	0.01039	$\pm$	0.00012	0.00148	$\pm$	0.00006
17	multi	1.0027	$\pm$	0.0023	0.01046	$\pm$	0.00013	0.00149	$\pm$	0.00005

Sample U3						Sample U4					
²³⁵ U/ ²³⁸ U	2σ	μg/g	2σ			²³⁵ U/ ²³⁸ U	2σ	μg/g	2σ		
4.394	±	0.125	12.0	±	1.1	5.890	±	0.135	19.4	±	2.7
5.478	±	0.114	13.1	±	1.2	6.246	±	0.115	17.9	±	2.4
4.282	±	0.101	13.4	±	1.3	5.707	±	0.111	17.6	±	2.4
3.971	±	0.106	11.6	±	1.0	6.092	±	0.114	16.1	±	2.2
1.911	±	0.079	4.4	±	0.4	1.904	±	0.053	8.3	±	1.1
3.158	±	0.088	12.2	±	1.0	3.924	±	0.076	11.9	±	1.6
4.092	±	0.096	11.8	±	1.1	2.956	±	0.055	11.1	±	1.5
4.326	±	0.100	11.4	±	1.0	2.938	±	0.061	10.7	±	1.5
6.779	±	0.178	18.7	±	1.7	4.317	±	0.115	12.4	±	1.7
4.901	±	0.108	10.4	±	0.9	5.102	±	0.124	15.8	±	2.1
4.469	±	0.110	10.6	±	0.9	5.435	±	0.123	12.4	±	1.7
6.114	±	0.191	8.5	±	1.1	5.859	±	0.130	13.8	±	1.9
4.476	±	0.119	10.6	±	0.9	5.162	±	0.144	13.4	±	1.9
3.076	±	0.058	11.2	±	1.0	4.669	±	0.101	13.1	±	1.8
0.413	±	0.026	3.5	±	0.3	3.047	±	0.080	11.2	±	1.5
1.154	±	0.033	4.8	±	0.4	5.847	±	0.148	14.5	±	2.0
0.241	±	0.010	4.1	±	0.3	2.462	±	0.070	9.0	±	1.2
0.899	±	0.056	5.6	±	0.5	3.314	±	0.075	7.1	±	1.1
2.627	±	0.079	9.5	±	0.9	2.113	±	0.049	4.7	±	0.6
3.042	±	0.078	15.7	±	1.5						
4.324	±	0.143	13.5	±	1.2						

Figure 1
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Figure 2
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Figure 4
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Figure 5

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Figure 6

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$^{234}\text{U}/^{238}\text{U}$

Figure 7

[Click here to download Figure: Fig 7- U236 Minor Is](#)

$^{236}\text{U}/^{238}\text{U}$

Figure 8

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Figure 9

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Figure 10

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Figure 11

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Figure 12

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Figure 13

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Figure 14

[Click here to download Figure: Fig 14 - Mixing Calculations](#)

Ms. Ref. No.: JENVRAD-D-15-00032

Title: Spatially-Resolved Analyses of Aerodynamic Fallout from a Uranium-Fueled Nuclear Test
Journal of Environmental Radioactivity

Thank you very much, to the editor and the reviewers, for taking the time and effort to review this paper. The comments were extremely thoughtful, well-put, and made the paper better. Below we have addressed each of the comments the reviewers have made. We have also largely rewritten the paper to be more clear and direct, following suggestions from both reviewers. Our comments are included below in bold (note all tables have been moved to the end of the manuscript):

Reviewer #1: I have a few general comments about this paper

1. The writing is overly wordy and difficult to follow at times, some specific examples are given below, but a re-write is suggested. **We've removed a number of sections and rewritten the others to focus on clarity.**
2. The author describe the application of several tools to analyze silicate spheres, but offer little discussion as to how these results would be novel in any sort of post-det forensics investigation. **Our goal is to better understand fallout formation, so we have removed the statements in the introduction discussing post-detonation forensics.**
3. The point of using a mixing model for forensics purposes is to gain insight to be weapon characteristics, ie, isotopics of fissile material. Because SIMS was not able to provide the necessary 234 numbers, this mixing model could not be used here. Instead the author assumes a value for the fissile material and uses the model to verify that the fallout spheres are in fact mixtures of dirt and bomb components. We already know this. **While it is known that fallout from U-fueled devices will contain a mixture of U from the soil and U from the device, the extent of mixing between soil and device debris has not been reported.**

Specific comments:

"Highlights section:

- The second bullet should be deleted; it adds no value and makes no sense. **We've rewritten the highlights section to clarify the main points of the study (lines 11-18).**

"Abstract"

- The writing here is extremely wordy and the author provides some uranium isotopic information out of context; if the paper is about simply making SIMS measurements, please just say that. **We've rewritten the abstract to be more clear and less wordy (lines 23-35).**

"Introduction"

The sentence beginning on line 62 "these observations..." is confusing...Trinitite has yet to be compared with observations from Trinity testing? **We have removed the double use of "observation" and clarified that trinitite has yet to be compared with aerodynamic fallout from Trinity (lines 74-76).**

Line 70 says the data collected was used to develop a simple model of fallout formation. Where?? **This statement referred to the mixing model. We've removed this statement and rewritten this paragraph to be more clear about the intent of the mixing calculations (lines 83-85).**

"Materials and methods"

Line 82, are the SEM images of coated particles? Could you please clarify why you needed to coat with so much carbon; typically we'd expect angstroms of material. **The carbon coater we use for electron microscopy, EPMA, and SIMS analyses coats with thicknesses on the order of 5-20 nm.**

Electron probe microanalysis is referred to as EPMA, EMPA and electron microprobe microanalysis throughout this document. This needs to be consistent. **We have amended the statements throughout the paper to refer to EPMA or electron probe microanalysis alone.**

Lines 153-160 are unreadable. This should be a table. **We put these results into a table (lines 186 and 198).**

"Results"

I disagree with your first sentence; the BSE images do not show a homogeneous composition. The rest of your paper contradicts this statement as well. **We have attempted to clarify our meaning by rewriting the statement. U1A and U1B contain some high Si regions and exhibit some degree of flow banding, but are free of large internal variations in compositions, such as those seen in U2 and U4 (lines 202-203).**

Line 162--SEM/EDS cannot verify the material is amorphous SiO₂ **We've amended the statement to reflect this (lines 206-207).**

Lines 215 and 216--are you able to make 234 and 236 measurements or not. Previously the paper says that this work was not able to make these measurements and all plots are of 235 and 238 only **Measurements made at LLNL were only able to measure 235 and 238. Measurements made at LANL were able to measure 234, 235, 236, and 238. We've added statements to help clarify this.**

The paper has two sections labeled "3.3", both of which would benefit from a re-write. Please clarify what the significance of the correlation between U isotope ratios and major element composition. **We've rewritten these sections to be more clear. We propose that the correlation between U isotope ratios and major element composition is evidence for molten agglomeration. While known, our results show that the U in these relatively large regions must have been incorporated into the two distinct melts before they agglomerated to form the final glass, which has not been reported (lines 346-353).**

"Discussion"

Many of the assertions made here are simply from literature, in particular, section 4.2 just seems to be a summary of known facts about fallout and not necessarily related to the data collected here. **While the formation of these glasses through the interaction of soil and device debris and subsequent collision of molten droplets is known, the observation that the different amounts of U mixed with relatively large molten droplets before they collided to form the final glass has not been reported (lines 346-353).**

Finally, this mixing model could be a very interesting part of this work; unfortunately, by making assumptions as to the uranium isotopes used in the weapon, the authors negate any applicability of this work. Essentially, the authors demonstrated that the spheres are inhomogeneous mixtures; this is not a publishable conclusion. **Our aim for the mixing calculations was to quantify the extent of mixing between the enriched and natural U end-members to better understand how much unfissioned fuel from the device is incorporated into these glasses and how it is distributed.**

This paper should be redrafted using concise, clear language. Further, discussions as to the potential usefulness of spatially resolved analysis should be clarified. The authors should revisit the data to demonstrate a more useful application of the mixing model present. **We have redrafted the paper to be more clear and concise and have attempted to clarify the usefulness of these spatially-resolved techniques by elaborating on how these techniques improve our understanding of fallout formation, which, admittedly, was not clear in our last version of the paper. We have shown that not only are these glasses heterogeneous with respect to U isotopes (a known conclusion), but remarkably homogeneous, a conclusion that has never been reported. We have also shown that U from the device mixed with relatively large melts of dissimilar major element composition before agglomerating and attempting to mix, which has never been reported. Furthermore, the extent of the U heterogeneity (mixing between U in the soil and U from the device) within glasses of this morphology has**

never been previously quantified. Unfortunately, to publish this paper openly, we are unable to perform further analyses with the mixing model. This is a situation we regret, but we believe the mixing calculation shown still shows something important and previously unknown.

Reviewer #2: Line 133: Define "useful" precision. **We've removed this statement. The minor isotopes are below the detection limit of the LLNL instrument when it is operating at high mass resolving power.**

Lines 135-136: Is this the same standard being doped with U described in lines 148-160? If it is make that clear. If not, why is it appropriate to use this standard for U concentration analyses but not the other, what IS this standard anyway? Is it traceable to any other standards; what is its composition and the associated uncertainties of that composition? Also why not use the aluminosilicate glass standard as an isotopic standard or vice versa? **We've rewritten this section to make it more clear. At LLNL, we used the same ~350 ppm aluminosilicate standard for the isotopic analyses and concentration data. The standard was produced at LLNL according to procedures in Appendix A. The U used to dope the standard was NBL CRM U500. However, there was likely a slight contamination in the fabrication process, so we have used the MC-ICP-MS measurements of these glasses as the correct U isotopics to determine the instrumental mass bias of our measurements (Appendix A).**

Lines 148 through 160: Greater description is needed of the doping process in regards to the method used as well as the U homogeneity/heterogeneity of the final glass. What was the mass and uncertainty of the U added to the glasses and what was the glass mass? Define "roughly equivalent to U500." Traceability of the standard being used to correct for instrumental bias in SIMS analyses needs to be established. This could be done if the "roughly equivalent" U500 isotopic ratios are known and listed. The reported isotopic ratios from the two standards deviate from U500 (http://science.energy.gov/~media/nbl/pdf/price-lists/certificates/CRM_U500_10_Milligram_Sample_Size_March_2008.pdf) in the range of -38‰ to -26‰ and -5‰ to +2‰ per mil, respectively, and their deviation from the bulk U used as a dopant should be reported. Also U500 is no longer a NIST standard; it is created, certified, and distributed through New Brunswick Laboratory. **We have rewritten this section to clarify these points. We now list the U isotopic ratios of the standard glasses and have added an appendix discussing how they were made (Appendix A). We also provide a table (Table A1) where we list the deviations from the certified values of CRM U500. In addition, we assert that the precision of the SIMS measurements on the standards serve to illustrate the homogeneity of the final glasses.**

More detail is needed in regards to the use of ICP-MS to analyze the prepared standard's U isotopic ratios. The authors did not state whether this was done with the standard in the same physical state as during SIMS analyses or if it was dissolved and analyzed as a solution. Furthermore the technique of ICP-MS is extremely vague. Was this MC-ICP-MS? Quadrupole, magnetic sector? More detail is required here. **We have elaborated on the methods in Appendix A (lines 536-539).**

The results obtained from ICP-MS analysis of the two standards need more information. It is not clear what standards were used to correct for instrumental mass bias resulting from the analysis method. Further, the number of analyses obtained to create these ratios and their uncertainties needs to be listed. Also it is unclear if these uncertainties are 1s or 2s. **We have elaborated on the methods in Appendix A (lines 536-539).**

Finally the reported percentages for "reproducibility and accuracy" are confusing. Are they a measure of the accuracy of the reported isotopic ratios obtained via SIMS analyses compared to ICP-MS? Or are they a descriptor of the reproducibility of multiple (not reported how many) analyses obtained via SIMS on the standard. It is interesting that there is worse "reproducibility and accuracy" in multi-collector mode compared to single collector, typically the reverse is true. Additionally count rates or voltages are never described for any of the reported measurements. **We have changed the phrase reproducibility to precision, which we present as the relative standard error of the mean of standards measurements via SIMS. We also elaborate on what we mean by accuracy, that is, the percent deviation of the mean of the SIMS standards measurements to the values measured via MC-ICP-MS (Table 2). We have included typical count rates for the measurements at both LANL and LLNL (lines 150-155 and 175-179).**

Line 179: Perhaps specify radioactivity here instead of activity since this is the first time it has been mentioned in a while. **We have replaced 'activity' with 'radioactivity' (line 239).**

Line 234: State the high $^{235}\text{U}/^{238}\text{U}$ ratio here. **We have stated the high $^{235}\text{U}/^{238}\text{U}$ ratio here (line 277).**

Line 241: Do you mean heterogeneity? The larger standard deviations in Ca and $^{235}\text{U}/^{238}\text{U}$ in U3 compared to U1A implies that there are more variations in U3 compared to U1A. **We have replaced 'homogeneity' with 'heterogeneity' (line 288).**

Lines 243 and 244: State what the resulting standard deviation would be without the low values near the center of U3 to justify your statement. **We have added this value to the statement (line 292).**

Line 262: Why do you have an assumed uncertainty for a standard? Analyze the standard and determine its uncertainty directly or use the documented uncertainty of the standard itself instead of guessing a value. **We have measured the concentration of U in our standard glasses and adjusted the uncertainties and calculated concentrations in the fallout glasses accordingly (line 186, table at end of paper, and Appendix B).**

Line 267: Figure 1 should not be repeated in this manuscript. **This was a mistaken figure label that we've corrected.**

Line 315: Using R2 values here is not the correct method to show a trend with the U3 data set, especially when your R2 value is 0.50. Perform other statistical tests to prove your point or remove the statement. **We've treated the data set as a whole to illustrate the correlation with concentration (lines 308-309).**

Line 316: Figure 3 does not show this. **This was a mistaken figure label that we've corrected.**

Line 331: How many uncertainties are they within each other? Quantify this statement. **We've rewritten this section to be more clear and this portion was removed. The data were fit collectively.**

Lines 319 through 327: Is it possible to state definitively what the ^{235}U enrichment was for the device? **We cannot make that statement based on the data we've collected.**

Table 3: Be consistent with sig figs in uncertainties. **We have made this correction.**

Figure 13: Nowhere in the entire article is there a reference to which concentration data points are paired up with U isotopic ratios. There are 20 concentration results in Table A for U3 and 22 isotopic ratios from LLNL in Table 3. A similar discrepancy exists with the U4 data. **At LLNL, we measured U isotopic ratios in 22 locations on spherule U3. However, the first measurement was in a location of low Si and high Ca content, visible on the right periphery of spherule U3 in the Ca map (Figs. 2 and 3). Determining the concentration of U relies on the ion signal of the measured matrix element (Si) being relatively constant amongst the analyses. Because the major element composition of the spherule in this location was grossly different than the rest of the glass, this point was excluded when we calculated the U concentrations. One other point was excluded erroneously; we have added it back in. All of the measurements from U4 were included. We've also included the U isotopic ratios that correspond to these concentration measurements to clear up any confusion.**

What logic was used to combine the concentration data points with the U isotopic ratios? **We plotted the U isotopic ratios and the concentration data together to illustrate that enriched U from the device dominates the U content in these glasses. These data also serve to illustrate that increases in U concentration are likely from the addition of enriched U.**

Also there is no description of the statistical treatment of the collected data to arrive at these concentration values. Did the authors account for decaying secondary ion count rate during the sputtering process or for duty cycle efficiency while the magnet was switching between masses 254, 251, 250.8, 30, and 29.8? No information is given regarding the magnet settling times or counting times for these measurements. **During the SIMS analysis, count rates remained relatively constant. The high voltage placed on the sample stage is periodically and automatically adjusted every 10-20 cycles (typically in steps of 10 V) during an analysis to keep the energy**

distributions of the secondary ions constant. This mitigates changes in secondary ion count rates as a result of the sputtering process. We also have provided typical counting and magnet settling times. The counting times are user-defined, whereas the magnet settling time is automatic and is determined by the difference in the magnetic field between successive masses, but is typically ~1 s.

Figure 14: What does "most" of the uncertainties are smaller than the points mean? Put the uncertainties on the plot and state that if the bars are not visible then they are within the data points. **This statement has been amended (lines 390-397).**

In addition a number of the guidelines to authors were not followed in regards to the figures and tables. The authors should return to the guidelines and make the appropriate changes. **The primary guideline with regards to figures that we realized was not followed was consistent fonts among all figures and vertical rules in tables. We have uploaded amended figures and reformatted our tables.**

In general the authors provide a striking lack of information regarding their sample measurement procedures and statistical treatment of their collected data. The subsequent conclusions drawn from their reported data seem logical, but the underlying validity and accuracy of their data appears to be suspect given the lack of detail into the way the data was collected and treated. I would advise a complete reanalysis of the samples and standards before resubmission. If there is adequate standard analysis data and the authors did treat their data in such a way to alleviate all of the above concerns then I strongly recommend that methodology be described in the text in enough detail that another scientist attempting to replicate their results and methods would be able to do so. **We've elaborated considerably on our standards, their measurements, and how measurements on the fallout glasses were made.**

Again, we thank you for your comments and insight and hope that we have addressed your concerns. We look forward to any further comments and your decision regarding publication.