Deposition of Vaporized Species onto Glassy Fallout from a Near-Surface Nuclear Test

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0. Abstract

In a near-surface nuclear explosion where the resultant fireball can interact with materials from the surface, vaporized materials from the nuclear device can be incorporated into molten soil and other carrier materials from that surface. This mixed material becomes a source of glassy fallout upon quenching and is locally deposited. Fallout formation models have been proposed; however, the specific mechanisms and physical conditions by which soil and other carrier materials interact in the fireball, as well as the subsequent incorporation of device materials with carrier materials, are not well constrained. We observe a surface deposition layer preserved at interfaces where two aerodynamic fallout glasses agglomerated and fused, and characterized 11 such boundaries using spatial analyses to better understand the vaporization and condensation behavior of species in the fireball. Using nanoscale secondary ion mass spectrometry (NanoSIMS), we identify higher enrichments of uranium from the device ($^{235}\text{U}/^{238}\text{U}$ ratio >7.5) in 8 of the interface layers. Major element analysis of the interfaces reveals the deposition layer to be enriched in Fe, Ca, Mg, Mn, and Na-bearing species and depleted in Ti and Al-bearing species. Most notably, the Fe and Ca-bearing species are enriched approximately 50% at the interface layer relative to the average concentrations measured within the fallout glasses, while Ti and Al-bearing species are depleted by approximately 20%. SiO_2 is found to be relatively invariable across the samples and interfaces ($\sim 3\%$ standard deviation). The notable depletion of Al, a refractory oxide abundant in the soil, together with the enrichment of ^{235}U and Fe, suggests an anthropogenic source of the enriched species or an unexpected vaporization/condensation behavior. The presence of

both refractory (*e.g.*, Ca and U) and volatile (*e.g.*, Na) species approximately co-located in most of the observed layers (within 1.5 μm) suggests a continuous condensation process may also be occurring. These fallout formation processes deviate from historical models of fallout formation, and have not been previously recognized in the literature.

1. Introduction

When a nuclear bomb is detonated near a surface, materials from associated structural materials and surfaces (including environmental debris such as soils) can be swept up into the ensuing fireball and interact with vaporized device material. As the fireball rises and cools, the entrained environmental debris can melt, incorporate radionuclides, and then quench, producing glassy fallout (Ross, 1948; Adams *et al.*, 1960; Glasstone and Dolan, 1977). The first observations of fallout glass were made after the Trinity nuclear test in New Mexico in 1945 (Ross, 1948). Subsequently, fallout was a subject of study over several decades to 1) understand how radionuclides are incorporated into fallout, and 2) to determine how radionuclides would be distributed over a geographic area following a nuclear explosion (*e.g.*, Adams *et al.*, 1960; Crocker *et al.*, 1965; Freiling, 1961; Miller, 1964). The physical and chemical processes through which device material and environmental debris interact to form fallout glass are not well constrained, but are critical for advancing the understanding of fallout formation. While models for the incorporation of radionuclides into fallout differ, there is consensus that fission products, unfissioned device materials, and vaporized inert materials are incorporated into molten silicate-rich spherical objects via condensation, convective mixing, and agglomeration (Freiling 1970; Miller, 1960; Izrael and Stukin 1970).

Formation of macro-scale fallout is a competitive process requiring carrier material interaction at the time of or shortly after the nuclear explosion (Glasstone and Dolan, 1977). Any near-surface nuclear explosion where the fireball rise time permits entrainment of materials from the environment (such as in a surface event, a tower event, or a low-altitude burst), or in shallowly buried events where the fireball can break the surface, can result in the formation of glassy fallout so long as the rising fireball interacts with proximate carrier materials prior to cooling below the Draper point ($\sim 525^{\circ}\text{C}$ for a black body radiator). In the seconds following a near-surface nuclear explosion, as the fireball expands, rises, and cools, vaporized material in the fireball may directly condense onto molten environmental debris and carrier materials, or may form condensates that subsequently deposit onto molten hosts. The resultant macro-scale materials generally settle out from the buoyant cloud within the first few hours, and are referred to as 'local' fallout.

Models of fallout formation suggest that the bomb vapor and resultant compositions trapped in the glassy fallout are affected by isotopic and chemical fractionation as the fireball evolves (Freiling, 1970). The fractionation process has been described in two phases based on the temperature regime and the state of carrier material (Miller, 1960). In the first phase, refractory fission products and residual actinides condense onto the surface of liquid carrier particles (such as melted environmental debris), and subsequently get incorporated into the particles through physical and chemical mixing processes. In the second phase, more volatile species condense onto the surfaces of solidifying carrier material (*i.e.*, quenched glass and unmelted environmental debris), resulting in an enrichment of volatile species at the surface relative to the average

particle composition. While such models capture a general picture of fallout formation, the contribution of environmental debris to the vapor phase and the effect of carrier materials on radionuclide distribution within individual objects and among fallout populations remain relatively unexplored.

Recent studies have shown that residual fission products and unfissioned actinides occur almost ubiquitously in fallout samples, and are heterogeneously distributed within and between fallout objects (*e.g.*, Eppich *et al.*, 2014; Lewis *et al.*, 2015; Fahey *et al.*, 2010; Bellucci *et al.*, 2013; Belloni *et al.*, 2011). Historical studies, using autoradiography to spatially determine gamma and beta-emitters in samples, found that a relative increase in the radionuclide activity on the surface of fallout objects is common (Miller *et al.* 1964, Adams *et al.*, 1960). Autoradiography cannot generally determine the identity of these radionuclides, however, and the spatial resolution of this technique is typically limited to tens of micrometers. While many of the high-activity species reported in historical studies have decayed away in the intervening decades, historical fallout retains a record of unfissioned actinides that can still be studied today. While chemical and isotopic variations within the outer layers of fallout objects are predicted, examination of the surface layers of fallout can be complicated by the analytical challenges of topographical edge effects that can produce artifacts in spatially resolved analytical techniques. In this study, we report for the first time that a surface deposition layer is preserved at the interfaces where molten objects have agglomerated, and we characterize the species deposited on these surfaces prior to collision and quenching. We then consider the implications these observations have for models of fallout formation.

Interfaces in agglomerated fallout glass, as we show, preserve a record of the interaction of device material and environmental debris as a distinctive chemical layer deposited on the surface of fallout objects prior to agglomeration. This study characterizes the vapor component in the fireball as represented by the unfissioned fuel, and addresses how these vaporized species interacted with molten environmental debris to form fallout glasses. We present high-spatial-resolution analyses of major elements and uranium isotopes across the interfaces of agglomerated fallout objects, which we then interpret in the context of thermal and temporal evolution of vaporized material in the fireball, competing fallout formation processes, and fireball heterogeneity.

2. Samples

Samples of agglomerated fallout glasses from a uranium-fueled, near-surface nuclear test were acquired within 600 meters from ground-zero (as presented in Eppich *et al.* (2014) and Lewis *et al.* (2015)). While aerodynamic fallout glasses from this event have been typically described as highly symmetric glassy beads (*i.e.*, spherical or otherwise rounded), for this study, five pieces of fallout were specifically chosen for their preservation of secondary objects fused to the host glass surfaces. All samples are mm-sized, aerodynamic glassy objects with multiple adhered smaller spheroids (Figs. 1 and 2). The 5 larger host objects are referred to as samples A, B, C, D, and E, while the smaller attached objects are referred to as Objects A1, B1, B2, B3, C1, C2, D1, D2, E1, and E2. In sample A, tens of secondary objects ranging in size from 5 to 500 micrometers can be observed fused to the larger host object. In the other 4 glassy samples (see

Electronic Annex 1 for images of all samples), fewer than five secondary objects (~100 micrometer-scale) were observed fused to each larger host sample (*e.g.*, Fig. 2).

The five glassy fallout samples were mounted in epoxy, polished to the mid-plane of the adhered spheroids to expose agglomerate interfaces, and coated with ~5 nm of carbon to enhance conductivity. Sample interfaces were then characterized by multiple analytical techniques (discussed below), including scanning electron microscopy (SEM) and electron probe microanalysis (EPMA), and NanoSIMS (nanoscale secondary ion mass spectrometry).

A collection of the local soil was also studied to provide context on the likely compositional protolith of the fallout. Approximately 20 composite, mm-scale grains were arbitrarily selected from a pre-sieved soil sample (1.68 mm mesh size) picked clean of observable fallout glass that had been acquired within 1 km of ground-zero, away from the direct path of the fallout plume. These soil grains were mounted in epoxy, polished to 1-micrometer surface roughness, and coated with a conductive carbon layer (~10 nm). The soil samples were characterized by SEM and EPMA.

3. Methods

3.1 SEM and EDS

An FEI Inspect-F Scanning Electron Microscope was used to acquire secondary electron images (SE) and back-scattered electron (BSE) images, using accelerating voltages of 5 kV and 15 kV, respectively. In Object A1, SE images were acquired to observe topographical features on the intact sample prior to polishing. BSE images were used to characterize the compositional variations in all the fallout samples and the

interfaces, based on relative BSE contrast variation in individual images. The mineral compositions and characteristic heterogeneity of the local soil was also characterized through BSE imaging of polished grain mounts. Further details of compositional variation of fallout objects and mineral phases are provided as supplementary material (Electronic Annex 1).

Semi-quantitative (standardless) major element composition profiles were acquired using an AMETEK EDAX Apollo XL Si drift energy dispersive x-ray spectrometer with an accelerating voltage of 15 kV. The profiles were acquired in traverses across the diameter of each analyzed fallout spherule along a path normal to the interface between fused objects, as well as across the interface into the larger host objects. The traverses consisted of 1 micrometer diameter analysis spots spaced approximately a micrometer apart, with a total of 7 interfaces characterized this way. The full EDS dataset is provided as supplementary material (Electronic Annex 4).

3.2 EPMA

Compositional maps and quantitative analyses of major elements in the soil grains and fallout glasses were acquired using a JEOL JXA-8200 electron microprobe. In fallout samples, compositional maps of Si, Al, Fe, Ca, K, and Na were acquired using 5 wavelength-dispersive spectrometers (WDS) and a JEOL silicon-drift energy dispersive X-ray spectrometer (EDS). These maps were acquired across selected small (100 to 400 micrometer diameter) attached spherules, including across the interfaces where these small objects fused to the larger host object. A total of 10 interfaces were characterized this way.

Quantitative composition profiles of major elements (presented here as the oxides SiO_2 , Al_2O_3 , FeO , CaO , K_2O , Na_2O , MgO , MnO , TiO_2) were acquired in traverses across the diameter of each analyzed fallout spherule along a path normal to the interface between fused objects, as well as across the interface into the larger host objects. The traverses consisted of 1 micrometer diameter analysis spots spaced 1.5 micrometers apart, with a total of 9 interfaces characterized this way. Each spot was acquired via WDS, with an accelerating voltage of 15 kV and a current of 10 nA. X-ray correction was performed using the CITZAF correction (Armstrong, 1995). For quantitative standardization, mineral standards comprising the oxide species of interest were analyzed using identical spectrometer and goniometer crystal settings as for the sample analyses; the specific standards were K-Feldspar (K, Al and Si); Fe_2O_3 (Fe); spessartine (Mn); rutile (Ti); diopside (Ca); albite (Na); and MgO (Mg). Under these conditions, the corresponding detection limits were 72 ppm for K, 173 ppm for Al, 162 ppm for Si, 294 ppm for Fe, 129 ppm for Ti, 118 ppm for Ca, 146 ppm for Na, and 146 ppm for Mg. Quantitative analyses were collected as element weight percent totals and converted to their corresponding oxide species using stoichiometric oxide conversion. In order to avoid topographical edge effects near the boundary between the sample material and the epoxy, only points more than 3 micrometers away from the edge were considered. The 1σ measurement uncertainties for major element spot analyses were <1% for Al, K, and Si, <5% for Na, Fe, Mg, and Ca, ~7% for Ti, and nearly 20% for Mn (see Electronic Annex 2 for full EPMA dataset).

Spot analyses in fallout samples were categorized regarding their proximity to the interface. Spots with local concentration maxima or minima observed co-located with

the relatively high-Z interface region identified by BSE images are designated as ‘interface points’, while all points not co-located with the high-Z interface are designated ‘interior points’, for the purposes of data discussion (see Electronic Annex 2 for full EPMA dataset for fallout glasses). Individual spot analyses were also acquired by WDS on the soil grain mounts to characterize the composition of the constituent phases of the soil material (see Electronic Annex 3 for full soil dataset). Spot analyses with totals less than 96% were discarded.

3.3 NanoSIMS

Ion images of 9 interfaces from 5 different glassy fallout samples were acquired with a *Cameca* NanoSIMS 50. A 200 pA primary $^{16}\text{O}^-$ beam with a spot size of ~ 750 nm was generated using the *Hyperion II* primary ion source (Oregon Physics). Secondary ions of $^{30}\text{Si}^+$, $^{54}\text{Fe}^+$, $^{44}\text{Ca}^+$, $^{235}\text{U}^+$, $^{238}\text{U}^+$, $^{235}\text{U}^{16}\text{O}^+$, and $^{238}\text{U}^{16}\text{O}^+$ were collected on 5 electron multipliers (except Sample A1, in which $^{56}\text{Fe}^+$ was measured instead of $^{54}\text{Fe}^+$); separately collecting $^{30}\text{Si}^+$, $^{54}\text{Fe}^+$, $^{44}\text{Ca}^+$, $^{235}\text{U}^+$ and $^{235}\text{U}^{16}\text{O}^+$ from $^{238}\text{U}^+$ and $^{238}\text{U}^{16}\text{O}^+$ by magnetic peak jumping. A mass resolving power ($M/\Delta M$) of $\cong 4000$ was used, sufficient to completely resolve interferences by $^{208}\text{Pb}^{27}\text{Al}$ (on ^{235}U) and $^{29}\text{Si}^1\text{H}$ (on ^{30}Si).

Instrumental mass fractionation of uranium isotopes and analytical variation over the course of the analyses were calibrated and quantified using spot analyses of both a matrix-matched glass standard, as well as a U_3O_8 standard. The ^{235}U -enriched glass standard was created at LLNL by fusing $\sim 5\%$ by weight of the CRM U100 U_3O_8 standard into a matrix of approximately 32% SiO_2 , 37% Al_2O_3 , and 31% CaO . CRM U100 has a certified $^{235}\text{U}/^{238}\text{U}$ ratio of 0.1136 ± 0.0001 . An $\sim 20\%$ ^{235}U enriched U_3O_8 particle

standard (CRM U200, certified $^{235}\text{U}/^{238}\text{U}$ ratio = 0.2512 ± 0.0003) was also used. The glass and U_3O_8 particle standards yielded measured percent deviations from the certified $^{235}\text{U}/^{238}\text{U}$ ratios of ~1.5% and ~2.5%, respectively.

Secondary ion images were acquired as $20 \times 20 \text{ } \mu\text{m}^2$ areas, with each image constructed from a series of 75-100, 256×256 pixel rasters (except Object A1, which was constructed from a $10 \times 10 \text{ } \mu\text{m}^2$, 128×128 pixel raster). Isotope ratio images of $^{54}\text{Fe}/^{30}\text{Si}$ (except Object A1, which used $^{56}\text{Fe}/^{30}\text{Si}$), $^{44}\text{Ca}/^{30}\text{Si}$, $^{235}\text{U}/^{30}\text{Si}$, and $^{235}\text{U}/^{238}\text{U}$ were generated from ion images, wherein the ratio image is an intensity map of an isotope ratio at each interface. Isotope ratio images were constructed using *L'image* software (Nittler, Carnegie Institution of Washington, Washington DC). Each image was smoothed using a 9-pixel (~0.6 micrometer) smoothing function (which approximated the NanoSIMS spot size applied for this study). In order to construct isotope ratio profiles, a 15-pixel wide (~1 micrometer) line was drawn normal to and across the interface between the two fused objects in each isotope image. The width of the line was selected to minimize the uncertainties in regions where count rates were low, while still accurately representing the variation of the isotope ratio across the interface. The 1σ measurement uncertainties for isotope ratios derived from the profiles were <1% for $^{44}\text{Ca}/^{30}\text{Si}$, $^{54}\text{Fe}/^{30}\text{Si}$, and $^{56}\text{Fe}/^{30}\text{Si}$, <5% for $^{235}\text{U}/^{30}\text{Si}$, and <10% for $^{235}\text{U}/^{238}\text{U}$ (see Electronic Annex 5 for full NanoSIMS dataset).

4. Results

4.1 Composition of soil material

The grain mounts of the soil material are primarily comprised of fine-grained granitic and rhyolitic clasts (mm-scale). The clasts primarily comprised quartz and feldspar, with lesser amounts of pyroxene and ilmenite. Feldspar compositions include both plagioclase (An₁₅-An₄₀) and alkali feldspar (Or₃₅-Or₆₅). These feldspar compositions are consistent with rhyolitic sediments. Pyroxene compositions were also observed, and include diopside and clinoenstatite. Table 1 shows the representative compositions of commonly observed minerals in the samples as acquired using EPMA spot analyses.

4.2 Relative heterogeneity and morphologies of fused glassy objects

Back-scattered electron images of polished fallout samples show a range of morphological and compositional characteristics in mm-scale host objects and smaller, adhered fallout spherules, as shown in Figure 3. The 5 larger (mm-scale) host objects to which the smaller objects are attached commonly have large vesicles (up to ~1 mm in diameter), as well as inclusions of what appear to be relict soil grains with diffuse boundaries based on major element composition (Fig. 3, Object D2).

Compositional heterogeneity of fallout glasses has been described in both trinitite (*e.g.*, Fahey et al. 2010, Bellucci and Simonetti 2012) and fallout objects from this test (Lewis *et al.*, 2015); however, the extent of compositional heterogeneity in sub-mm-scale objects has not been previously studied. In this study, the internal composition of the small, attached, glassy objects ranges from relatively chemically homogeneous (Fig. 3, Objects C1-3, E1) to distinctly heterogeneous (Fig. 3, Objects B3, D1, and D2). Vesicles (seen as dark black circles or ovals in BSE images) were most commonly observed in the samples showing the greatest degree of heterogeneity in major element composition.

Small patches, approximately tens of micrometers in diameter (*e.g.*, dark gray areas in Fig. 3, Object D2) were identified by EDS, and are nearly pure SiO₂ in composition.

The extent to which the smaller objects have been incorporated into larger objects varies (Fig. 3). For example, Objects C1 and C2 are two fused objects that have retained a highly spherical geometry, with the ratio of major and minor axes being ~1.07 in both cases. Object C3, on the other hand, appears flattened against the host object, having a ratio of major to minor axis of ~1.44, with the major axis measured at the widest point of the sample. This is further exemplified in Objects B1-3 (Fig. 3), where multiple stages of incorporation appear to be preserved; Object B3 has a flattened interface and has merged into the larger host, while sample B1 (left fused object, partially shown in Fig. 3) has only slightly merged with the central object. Between these two agglomerates, Object B2 is a smaller (~50 micrometer) object that is sandwiched between B1 and B3, and appears to have merged fully into the surface of B3.

One distinct feature present in all samples studied here, and of particular relevance to our findings, is seen at the interfaces of where the small glassy spheres (<1 mm) are attached to the larger objects. These interfaces appear as a thin, bright boundary in BSE images, suggesting these lines are regions of relatively higher average atomic number (Z) than the surrounding material (Fig. 3). Despite the range of morphologies and compositional variation observed in the agglomerated glassy fallout presented in this study, this high Z boundary feature is observed at every interface where the objects have fused together.

4.3 Major element composition of the interfaces

X-ray intensity maps (Fig. 4A), show that the high Z interfaces observed in the BSE images are part of a continuous layer that surrounds the smaller, attached objects, and appears enriched in Ca and Fe and depleted in Al relative to the average composition of the interiors of the smaller objects. The edges of objects adjacent to epoxy (shown in black) also appear to be enriched in Ca and Fe. Although this apparent enrichment at the sample edges could result from an artifact due to topographical edge effects, the continuity of this feature along agglomeration boundaries is strong evidence that the feature is intrinsic to the adhered objects. Object C2 in particular (Fig. 4A) shows a continuous, uniformly thick layer of Ca around the entire object adjacent to a region depleted in Ca. In 9 of the studied samples, the interface and exterior edge of the adhered objects is also enriched in Na, appearing as a thicker, more diffuse region when compared to the areas of Ca and Fe enrichment (*e.g.*, Fig. 4B). Samples with observable enrichment in Na at the interface and/or outer edge (as seen in X-ray intensity maps and EDS traverses) include A1, B1, B2, C1, C2, C3, D2, E1 and E2.

Major element traverses, presented in stoichiometrically corrected oxide form, show a chemical enrichment of Fe and Ca that is observed at nearly every interface, along with a corresponding depletion of Al and Ti relative to the interior. A typical relationship is shown in Fig. 5. These trends of relative elemental enrichment and depletion are also observed at the edge of the object, suggesting that the distinct compositional regions at the interfaces are part of a continuous layer around the smaller attached objects. The high beam current and small spot size necessary to acquire sufficient spatial resolution with sequential EPMA spot analyses for these traverses can result in volatilization of Na and K (up to 15% relative loss, see Electronic Annex 6). Taking this complication into account,

composition profiles of Na and K (*e.g.*, Fig. 4B) acquired by EDS show relative enrichment of Na in 5 of the 9 interfaces (A1, C1, C2, C3, and E1) and relative enrichment in K in 3 of the 9 interfaces (C1, C2, and E1).

The enrichments and depletions of major elements at the interface of fused objects can be best summarized by as the individual spot analysis corresponding to the local minima or maxima (Table 2). The average (or nominal) concentrations of the major elements determined from data collected immediately adjacent to the interface (three spot analyses on either side, see Table 2), show the relative enrichment or depletion of the major elements at the interfaces with respect to the interiors of the samples. Localized enrichments of Fe, Ca, Mn, and Mg (converted to oxides) are observed at all 9 measured interfaces, although the low abundances of Mn and Mg make quantification of these two elements difficult. Both Fe and Ca enrichments are observed to be ~50% relative to their corresponding nominal values observed on either side of each interface. A corresponding depletion of Al and Ti is also observed at all 9 interfaces measured with EPMA, with both elements depleted ~20% relative to the nominal values on either side of the minima for each interface (Table 2). Si did not show appreciable variation in the attached objects or interfaces; SiO₂ concentration has a standard deviation of 2.9% for the entire dataset.

Comparison of the interface values with the average object compositions shows that the observed concentration enrichments and depletions cannot be explained by compositional variation of the host objects. This is exemplified in the major element oxide plot of CaO and Al₂O₃ (Fig. 6A). The interior data vary by approximately 10% Al₂O₃ concentration (average value of $13.8 \pm 1.6\%$ Al₂O₃ by weight), and 2% by weight in CaO. All interface data fall below the average Al₂O₃ concentration of the object

interiors, with 7 of the interfaces greater than 1σ , and 4 of the interfaces greater than 2σ from the average value. While some interface data fall within 1σ of the average interior Al_2O_3 value, even these interfaces are depleted in Al_2O_3 when compared to the interior data points collected immediately adjacent to the local interface (Table 2). The CaO composition of the interfaces is generally enriched compared to object interiors (the average value is 2.0 ± 0.4 CaO by weight). Several of the interfaces are greater than 1σ , and 4 of the interfaces are greater than 2σ from the average CaO concentration of the interiors. Objects C2 and E1 have a lower concentration of CaO at the agglomerate interface. When compared to the immediately adjacent interior points, however, the interface of Object E1 is relatively enriched in CaO (Table 2).

Interfaces show a clear trend of enrichment in FeO (by as much as 55%) relative to object interiors (the average concentration of object interiors is $2.78 \pm 0.42\%$ FeO by weight). This is exemplified in the relationship between FeO and TiO_2 (Fig. 6B). Nearly all characterized interfaces are enriched in FeO concentration relative to the average interior FeO concentration (with the exception of B2), with 6 of the measured interface FeO concentrations greater than 2σ from the average interior concentration. Even at the interface of Object B2, the FeO concentration is 17% higher than the concentration measured immediately adjacent to its interface. The TiO_2 concentration in 8 of the 9 measured interfaces is depleted relative to the average concentration of the interior ($0.29 \pm 0.06\%$ TiO_2 by weight), with 4 of the measured interfaces having a TiO_2 concentration more than 1σ from the average concentration of the object interiors. In 6 of the 9 measured interfaces TiO_2 is depleted relative to the interior values by $>25\%$.

4.4 Isotopic compositions at interfaces

The isotope ratio images of $^{54}\text{Fe}/^{30}\text{Si}$, $^{44}\text{Ca}/^{30}\text{Si}$, $^{235}\text{U}/^{30}\text{Si}$, and $^{235}\text{U}/^{238}\text{U}$ show a relatively higher value of each isotope ratio in 8 of the 9 interfaces, as measured by NanoSIMS ion image generated maps. All nine boundaries show a high level of ^{235}U isotopic enrichment (>60%) relative to ^{238}U , and six of these show increased uranium concentration at the interface between two fused objects (*e.g.*, Figure 7; Electronic Annex 1). Further, the $^{54}\text{Fe}/^{30}\text{Si}$, $^{44}\text{Ca}/^{30}\text{Si}$, and $^{235}\text{U}/^{30}\text{Si}$ maxima are commonly observed to be spatially co-located (to within <1.5 micrometers) at the measured interfaces (*e.g.*, Fig. 8). These relationships are not ubiquitous, as the interfaces of Objects A1, B1, and B2 do not show a systematic enrichment at the interface (discussed below).

At the C1 interface, the $^{54}\text{Fe}/^{30}\text{Si}$ and $^{44}\text{Ca}/^{30}\text{Si}$ isotope profiles across the boundary with the host object are consistent with the EPMA oxide data for Fe and Ca (Fig. 7). Table 3 presents the isotope ratio variation of $^{54}\text{Fe}/^{30}\text{Si}$, $^{44}\text{Ca}/^{30}\text{Si}$, $^{235}\text{U}/^{30}\text{Si}$, and $^{235}\text{U}/^{238}\text{U}$ across the interface of Object C1, as shown in Figure 7. The $^{235}\text{U}/^{30}\text{Si}$ profile at this boundary indicates a pattern of high $^{235}\text{U}/^{30}\text{Si}$ ratio at the interface having a quasi-Gaussian shape, similar to that of Fe and Ca as measured by both EPMA and NanoSIMS. The $^{235}\text{U}/^{30}\text{Si}$ ratio at the interface increases 10-fold, from a baseline value of approximately 10^{-4} to approximately 10^{-3} (Table 3). At approximately the same location as the maximum $^{235}\text{U}/^{30}\text{Si}$ value, the $^{235}\text{U}/^{238}\text{U}$ ratio of the C1 interface also has a local maxima at the interface with a value of ~7.5, compared to a value of ~6 on either side of the interface (Table 3).

The enrichment pattern at the B2 interface differs notably from the other samples in this suite. Object B2 shows a characteristic enrichment of $^{54}\text{Fe}/^{30}\text{Si}$ and $^{44}\text{Ca}/^{30}\text{Si}$ at the

interface, as otherwise observed in the sample suite. However, unlike the rest of the objects in this sample suite, a sharp compositional boundary between a region of higher and lower $^{235}\text{U}/^{30}\text{Si}$ ratio is observed at the B2 interface (Fig. 9). In contrast, the B1 interface, while attached to the same host object, shows the characteristic enrichment of $^{235}\text{U}/^{30}\text{Si}$ observed in all the other investigated interfaces (Fig. 9).

5. Discussion

5.1 Thermal histories preserved in agglomerated fallout glasses and their implications

The average composition of these fallout glasses is compositionally similar to local environmental materials (*e.g.*, Eppich *et al.*, 2015; Table 1). When characterized at the sub-mm-scale, however, these fallout glasses reveal significant textural and compositional heterogeneities. Larger (mm-scale) host objects preserve evidence of mechanical mixing (such as composition flow textures), variable degrees of vesiculation, eccentric (non-spherical) shapes, and inclusion of vitrified relict grains (in these samples, areas of nearly pure SiO_2 with diffuse boundaries, Fig. 3). The brightness and contrast of BSE images was adjusted at the time of collection to highlight unique features in each individual sample, preventing direct comparison of the contrast between images. Within-image contrast between host objects and agglomerates captured in the same BSE image, however, can be used to characterize general composition features. Among the studied population of agglomerated objects examined here, several attached objects are relatively chemically homogeneous in comparison to their respective host objects, based on the

relative contrast variation in individual BSE images (see Figs. 3 and 10). This observation suggests that these smaller objects were not only molten long enough to acquire a spherical shape through surface tension, but were also heated to sufficient temperature long enough to allow for homogenization of the probably multi-mineralic soil precursor through a combination of mixing and/or diffusion.

The relative homogeneity of small agglomerated objects (as compared to their host objects) provides a metric by which individual agglomerated objects can be compared. For example, Object D2 is the most compositionally heterogeneous (i.e. very similar contrast variation to the larger host of sample D), while Object C1 is relatively homogeneous when compared to the larger host object of sample C (Fig. 10). Given that D2 and C1 are approximately the same size (~250 μm and ~200 μm in diameter, respectively), a comparable level of homogeneity would be expected assuming identical starting composition and temperature history. Object D2 shows evidence of relict quartz and has preserved flow textures, suggesting internal advection or mechanical mixing, while these features are absent from Object C1. The observed variability in the degree of compositional homogeneity between agglomerated objects suggests that these individual objects were exposed to variable degrees of heating and/or duration of heating.

The degree of deformation and coalescence of small objects after collision with larger objects is also indicative of the thermal history of glassy fallout agglomerates. In Objects C1-3 (Fig. 3), C1 and C2 experienced little deformation from ideal sphericity upon collision with the larger object, while C3 has coalesced with the larger object. In Object C2, the larger host, sample C, appears to wrap around the exterior of the smaller object to some extent. This suggests that the smaller object was more viscous than the

host object, though surface tension and collisional velocity also affect the outcomes of liquid droplet collisions (Qian and Law, 1997). While droplet interaction parameters were not quantified in this study, viscosity increases more than 1000-fold for glass compositions similar to fallout from 2000 K to 1500 K (calculated from Giordano *et al.*, 2008), and the degree of deformation and coalescence may reflect the thermal dissimilarity between objects. The timescales at which surface closure to mass transfer occurs in glasses of these compositions (~1500 K) has been quantified in mm-scale objects from a single event to range from <0.1 to 2.9 seconds (Cassata *et al.*, 2014). This variation is attributed to both thermal variation in the fireball and the trajectory of entrained material through the fireball. Thus, as collisions between agglomerated objects occurred in the fireball, the range of thermal histories experienced by similarly sized fallout objects indicates thermal heterogeneity in the fireball and/or a difference in duration of heating for individual objects. In either or both cases, the presence of a deposition layer at every observed interface suggests that a continuing condensation processes (or deposition of condensates onto the surfaces of molten carrier materials) occurs over a range of times and/or temperatures in the fireball.

5.2 Interpreting enrichments of device material at interfaces

Using high-spatial-resolution analytical methods such as NanoSIMS to probe the interfaces of agglomerated fallout glasses, we observed an increase in ^{235}U relative to the interior of micrometer-scale objects. The ubiquitous presence of enriched levels of ^{235}U in these fallout glasses confirms that significant mixing of device material with environmental debris occurs during glass formation (Eppich *et al.*, 2014, Lewis *et al.*,

2015). Both historical autoradiography studies and modern spatial studies, however, show that the mixture of device material into fallout is not a uniform process. SIMS analyses (Lewis *et al.*, 2015) have demonstrated variation in $^{235}\text{U}/^{238}\text{U}$ over 2-3 orders of magnitude in single objects. More interesting to this study, enrichment of active beta emitters (such as ^{90}Sr and other fission products) has been observed as a surface layer on fallout objects (Crocker *et al.*, 1965, Adams *et al.*, 1957). While we can no longer characterize shorter-lived nuclide distributions in these materials (US atmospheric nuclear activity concluded with the end of the Plowshare program in 1977, and thus any shorter-lived radionuclides have since decayed), we postulate that historically reported surface features may correspond with the surface layer we observe preserved at the interface of agglomerated objects. In our analyses, local enrichments of ^{235}U are correlated with increased iron and calcium concentration in nearly every sample (*e.g.*, Figs. 7 and 8), suggesting that these species co-condensed, depositing together.

The $^{235}\text{U}/^{238}\text{U}$ ratios at the characterized interfaces of agglomerated objects indicates that the vast majority of the uranium in the deposition layer observed in this sample suite is not natural in origin, but instead derived from residual device fuel. It is expected that a fraction of other local material proximate to the device (such as soil and associated structural materials related to the staging of the nuclear test) would have also been vaporized in the initial explosion. Vaporization of soil and other local materials is the most probable source of the other observed chemical enrichments in the interface layers. The observed co-locations of $^{44}\text{Ca}/^{30}\text{Si}$, $^{54}\text{Fe}/^{30}\text{Si}$, and $^{235}\text{U}/^{30}\text{Si}$ enrichments (*e.g.*, Fig. 8) are most simply interpreted as the result of Fe and Ca from the soil and/or anthropogenic components vaporizing together with the device fuel, and subsequently

forming a direct condensate from the vapor state or depositing onto the carrier materials as a condensed species.

5.3 Depletion of Al and Ti at the interface

Agglomerate interface layers are consistently depleted in Al and Ti, along with relative enrichment of Fe and Ca (Fig. 6). Al and Ti are relatively refractory elements that are abundant in the soil material from which such fallout carrier material is most likely derived (Table 1). The boiling points of oxides found in the soil provide a simple metric by which to compare their relative volatilities in complex silicate matrices. Given the similarity in boiling points of FeO, TiO₂, CaO, and Al₂O₃ (2785 K, 3273 K, 3100 K, and 3250 K, respectively: Cornell and Schwertmann, 2003; Haynes, 2015; Patnaik, 2003) and the occurrence of FeO with TiO₂ and CaO with Al₂O₃ in major mineral phases (*i.e.*, ilmenite and plagioclase, see Table 1), it might be expected that these species would enter the vapor phase together, condensing proportionally onto molten carrier materials. However, boiling points may be a poor proxy for estimating vaporization behavior of these species out of a complex silicate such as the proximate soils. One possible explanation for the observed depletion of Al and Ti at our interfaces is that Al and Ti did not enter the vapor phase with Fe and Ca, as might expected based on their boiling points and co-occurrences in their respective common mineral phases (Al, Ca in plagioclase and Fe, Ti in ilmenite), making these elements less available for interaction with molten carriers in the fireball. This interpretation is unlikely, however, as CaO is approximately as refractory as Al₂O₃ in a molten silicate system similar to that found in fallout samples (Walter and Giutronich, 1967).

Fractionation between species may instead be dictated by the condensation behavior within the fireball environment. Condensation temperatures for Ca, Ti, and Al are calculated by Lodders *et al.* (2003) are reported to be within ~100 K of each other. These values are calculated for elements condensing out of a solar composition gas in equilibrium, however, rather than for fireball conditions, which may be significantly different. While historical fallout formation models assume a highly oxygenated fireball (*e.g.*, Miller, 1960), the study by Cassata *et al.* (2014) provides evidence of a reducing fireball environment during fallout formation. The speciation of vaporizing constituents can change depending on oxygen fugacity and temperature (Lamoreaux *et al.*, 1984 and Lamoreaux *et al.*, 1987). Such changing conditions would not only affect the composition of the vapor phase, but would also affect the condensation behavior of these constituents.

Silicate soils are unlikely to be the sole source of elements in a fireball vapor due to the abundance of other structural and instrumentation material that may have been placed in the near field for historical nuclear tests. Recent studies of fallout debris from the Trinity test (trinitite) identify unusual chemical and isotopic enrichments as signatures attributed to support structures, unfissioned fuel, and other, non-fuel device components (Fahey *et al.*, 2010; Bellucci *et al.*, 2014; Donahue *et al.*, 2015; Eby *et al.*, 2015). Thus, an alternative explanation for the Ca enrichments observed at the interfaces may be the presence of an anthropogenic source (*e.g.*, structural materials, such as common cement having >60% CaO) proximate to the device prior to the explosion that significantly contributed to the vapor phase, rather than simple derivation from local soil material (~1.5 wt% CaO, Eppich *et al.*, 2014). While aluminum is also a common constituent of

concrete aggregates, the relative aluminum content of potential anthropogenic structures external to the nuclear device prior to explosion can vary considerably, and is unknown for this location. Similarly, the excess Fe observed at the interfaces within these samples may also derive from significant vaporization of Fe-bearing component (*i.e.*, steel). The observed pattern of enrichments and depletions at the interfaces may therefore reflect, in part, relative contributions of proximate structural materials, manifesting as an apparent depletion of aluminum relative to iron, calcium, and uranium in the vapor phase. Further determination of the volatilization and condensation behavior of these species will be necessary to differentiate between these hypotheses.

5.4 Co-location of volatile and refractory species at the interface

Historical models of fallout formation present a two-stage fractionation sequence for the incorporation of vaporized species into molten carriers. Specifically, these models argue that in a first stage refractory species (including uranium) are expected to condense early and distribute volumetrically into molten host materials, while in a second, later stage, more volatile species are expected to condense and deposit on the surface of already solidified hosts (Freiling 1970; Miller, 1960; Izrael and Stukin 1970). In a silicate system of composition similar to that of these fallout objects (Walter and Giutronich, 1967), Al_2O_3 and CaO would be considered the most refractory species, while K_2O , SiO_2 , and Na_2O would be the most volatile. If the condensation sequence was dictated by the relative volatility of individual vaporized species, we would expect to see a distinct separation of refractory oxides from volatile oxides. This would manifest as a higher relative concentration of refractory species (*e.g.*, Ca and Al from the environmental

debris, ^{235}U from the device) volumetrically distributed inside of the glassy fallout objects, and a post-quenching surface-deposited layer of volatile species (*e.g.*, enriched in Na_2O , K_2O derived from vaporization of the local soil). Instead, as observed at these interfaces, enrichments of both refractory (Fe, Ca, Mg, Mn, and ^{235}U) and volatile species (Na) are observed to be co-located at the interfaces in more than half of the studied samples, while Al is depleted at this boundary in all the samples. The presence of a layer enriched in both refractory and volatile species deposited onto molten soil carriers that have already encountered and incorporated a device-material bearing vapor phase does not fit well into a two-stage interaction model dictated by oxide species volatility such as that proposed by Miller (1960).

Two possible explanations can account for the presence of the observed interfaces: 1) The deposition layer reflects continuous condensation and mixing based on the volatility of species in the vapor, where speciation may be complex and/or changing under the rapid cooling conditions of the fireball vapor, and/or 2) Molten carrier materials interacted with a compositionally and thermally heterogeneous fireball vapor, with later interactions encountering a compositionally different (for example, Al-depleted) vapor. Norman and Winchell (1966) first proposed a model of continuous condensation and diffusion to explain observations of incorporated fission products, in contrast with the model of Miller (1960) where refractory species condense early and mix volumetrically, while volatile species deposit onto an already frozen particle without being appreciably incorporated into the object. Continuous profiles of vapor-derived species, where a single, continual concentration gradient between host and agglomerated object is preserved on either side of the interface, were not always observed in our study. As

shown in the $^{235}\text{U}/^{30}\text{Si}$ ion ratio images of the agglomerate interfaces of Objects A1 and B3 (Electronic Annex 1 and Fig. 11, respectively), as well as the qualitative EPMA map of the Ca distribution in Object C2 (Fig. 4A), continuous concentration profiles appear rare for every element characterized in this study, with the exception of Si. This observation is exemplified in Fig. 11, where the $^{235}\text{U}/^{30}\text{Si}$ isotope ratio image shows a distinct layer of ^{235}U at the interface between two objects. While zones of relative ^{235}U depletion can be seen on either side of the local ^{235}U maxima, it is one of the depleted zones which hosts the local maxima for $^{54}\text{Fe}/^{30}\text{Si}$.

The presence of a relatively high $^{235}\text{U}/^{30}\text{Si}$ region adjacent to a relatively low $^{235}\text{U}/^{30}\text{Si}$ - high $^{54}\text{Fe}/^{30}\text{Si}$ region can be best explained by a discontinuous evaporation and condensation process. For example, if the molten carrier objects passed through a vapor in the fireball having a negligible uranium concentration (*i.e.*, not well-mixed with device material) but significant iron concentration, the partial pressure of U would favor an evaporative process, resulting U loss from the soil-derived host material, but permitting significant deposition of Fe. Subsequently, if debris then passed through a vapor having high uranium concentration (*i.e.*, well-mixed with and dominated by vaporized device material), the partial pressure of U would favor a condensation process, depositing a layer of uranium with higher relative ^{235}U . If the trajectory of the fallout debris brought it through a relatively cooler region of the fireball that had become more concentrated in volatile species, it is possible that these species could also condense onto and diffuse into the still-molten fallout object. Given the variation in relative enrichment and depletion of species observed at the interfaces, our study suggests that a combination of these processes is likely to be occurring.

5. Conclusions

We identified a set of micrometer-thick compositionally distinct surface layers in fallout, best preserved as boundaries between agglomerated glassy fallout objects. Using a combination of spatially resolved analytical techniques, we determined the major element and uranium isotopic compositions of the observed deposition layers, and their relative enrichments or depletions with respect to the object interiors and host object compositions. While the interior composition of glassy fallout objects more closely matches the major element composition of local soils, the composition of the boundary layers does not resemble any particular mineral phase or the average soil composition. Relative to the bulk (interior) compositions of the attached objects, the interface layer is enriched in ^{235}U , indicating that the deposition layer is enhanced in device material. The correlation of ^{235}U enrichment with relative enrichment of Fe and Ca at these interfaces indicates mixing with vaporized species from the soil or proximate anthropogenic structural material, and preferential condensation. A notable depletion of refractory Al and Ti at the interface, species abundant in the soil, complicate this interpretation. The Al and Ti depletion at these interfaces is unlikely to be due to preferential evaporation from the sample surfaces, but may be indicative of an anthropogenic source (*e.g.*, the device or structural materials related to the staging of the event). These patterns of enrichment and depletion may also be attributed to or enhanced by unexpected vaporization/condensation behaviors of species in the fireball. In order to more comprehensively understand these behaviors, it will be necessary to study the speciation

of these elements, and their vaporization and condensation behaviors in controlled environments representing fireball conditions.

The observed interface layers are also frequently enriched in volatile species such as Na and K. This observation is best explained by a continuously occurring condensation-diffusion process while the fallout objects were entrained in the fireball, rather than by a two-step deposition process that would have fractionated volatile and refractory species. Observed regions of enrichment and depletion for uranium within individual samples point to either heterogeneities in fireball vapor composition, where vaporized materials from environmental debris and the device were not well mixed, and/or competing vaporization-evaporation processes affected by local gradients of already deposited species.

Regardless of the specific mechanisms, the observed surface and interface layers were clearly deposited after the carrier material melted, but prior to agglomeration and quenching. Previous studies of these materials show that the entire volume is variably enriched in uranium concentration as well as isotopic ^{235}U , relative to natural values (Eppich *et al.*, 2014, Lewis *et al.*, 2015). If species in the vapor phase interacted with carrier materials in a continuous condensation-mixing process, the species present in the fireball vapor must have volumetrically interspersed through the molten carrier via diffusion and/or physical mixing processes prior to deposition of the surface layer characterized in this study. Quantifying diffusion profiles at the interface can provide further insight into the range of timescales and temperatures these fallout objects experienced in the fireball prior to quenching, and is the subject of concurrent research.

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7. References

Adams C. E., Farlow N. H. and Schell W. R. (1960) The compositions, structures and origins of radioactive fall-out particles. *Geochimica et Cosmochimica Acta* **18**, 42-56.

- Adams C. E. and O'Connor J. D. (1957) The Nature of Individual Radioactive Particles, VI: Fallout Particles from a Tower Shot, Operation Redwing.
- Armstrong J. T. (1995) CITZAF: a package of correction programs for the quantitative electron microbeam x-ray analysis of thick polished materials, thin films, and particles. *Microbeam Anal.* **4**, 177-200.
- Belloni F., Himbert J., Marzocchi O., and Romanello V. (2011) Investigating incorporation and distribution of radionuclides in trinitite. *J. Environ. Radioact.* **102**, 852-862.
- Bellucci J. J., Simonetti A., Koeman E. C., Wallace C. and Burns P. C. (2013) A detailed geochemical investigation of post-nuclear detonation trinitite glass at high spatial resolution: Delineating anthropogenic vs. natural components. *Chem. Geol.* **365**, 69-86.
- Cassata W. S., Prussin S. G., Knight K. B., Hutcheon I. D., Isselhardt B. H. and Renne P. R. (2014) When the dust settles: stable xenon isotope constraints on the formation of nuclear fallout. *J. Environ. Radioact.* **137**, 88-95.
- Crocker G. R., O'Connor J. D. and Freiling E. C. (1965) Physical and Radiochemical Properties of Fallout Particles. US Naval Radiological Defense Laboratory, USNRDL-TR-899.
- Donohue P. H., Simonetti A., Koeman E. C., Mana S. and Burns P. C. (2015) Nuclear forensic applications involving high spatial resolution analysis of Trinitite cross-sections. *J. Radioanal. Nucl. Chem.* **306**, 457-467.
- Eby G. N., Charnley N., Pirrie D., Hermes R., Smoliga J. and Rollinson G. (2015) Trinitite redux: Mineralogy and petrology. *American Mineralogist.* **100**, 427-441.

- Eppich G. R., Knight K. B., Jacomb-Hood T. W., Spriggs G. D. and Hutcheon I. D. (2014) Constraints on fallout melt glass formation from a near-surface nuclear test. *J. Radioanal. Nucl. Chem.* **302**, 593–609.
- Fahey A. J., Zeissler C. J., Newbury D. E., Davis J. and Lindstrom R. M. (2010) Post-detonation nuclear debris for attribution. *Proc. Natl. Acad. of Sci.* **107**, 20207–20212
- Freiling E. C. (1961) Radionuclide Fractionation in Bomb Debris. *Science* **133**, 1991-1998.
- Freiling E. C. (1970) Mass-Transfer Mechanisms in Source-Term Definition. In *Radionuclides in the Environment*. American Chemical Society, Washington, D.C. pp. 1-12.
- Glasstone S. and Dolan P. J. (1977) The Effects of Nuclear Weapons. US DOD and US DOE. US Government Printing Office: 1977 O-213-794, Washington, D.C.
- Haynes, W. M (Ed.). (2015-2016) *CRC Handbook of Chemistry and Physics*. 96th ed. CRC Press: Boca Raton, FL.
- Izrael Y. A. and Stukin E. D. (1970). Production of Radioactive Fallout. In *The Gamma Emission of Radioactive Fallout*. US Atomic Energy Commission and NSF, Washington, D.C. pp. 1-46.
- Lamoreaux R. H. and Hildenbrand D. L. (1984) High Temperature Vaporization Behavior of Oxides. I. Alkali Metal Binary Oxides. *J. Phys. Chem. Ref. Data.* **13**, 151-173.
- Lamoreaux R. H., Hildenbrand D. L. and Brewer L. (1987) High-Temperature Vaporization Behavior of Oxides II. Oxides of Be, Mg, Ca, Sr, Ba, B, Al, Ga, In, Tl, Si, Ge, Sn, Pb, Zn, Cd and Hg. *J. Phys. Chem. Ref. Data.* **16**, 419-443.

- Lewis L. A., Knight K. B., Matzel J. E., Prussin S. G., Zimmer M. M., Kinman W. S., Ryerson F. J. and Hutcheon I. D. (2015) Spatially-resolved analyses of aerodynamic fallout from a uranium-fueled nuclear test. *J. Environ. Radioact.* **148**, 183-195.
- Lodders K. (2003) Solar System Abundances and Condensation Temperatures of the Elements. *The Astrophysical Journal*. **591**, 1220-1247.
- Mehta P. K, Monteiro PM (2006) *Concrete: microstructure, properties, and materials*. McGraw-Hill, New York.
- Miller C. F. (1964) *Biological and Radiological Effects of Fallout from Nuclear Explosions*. Stanford Research Institute, Menlo Park, CA.
- Miller C. F. (1960) *A Theory of Formation of Fallout from Land-surface Nuclear Detonations and Decay of the Fission Products*. Naval Radiological Defense Laboratory, San Francisco, CA.
- Norman J. and Winchell P. (1966) Cloud Chemistry of Fallout Formation. *Proceedings of the Fallout Phenomena Symposium 1966*. pp. 12-54.
- Patnaik P. (2003) *Handbook of inorganic chemicals (Vol. 28)*. McGraw-Hill, New York.
- Qian J., Law C. K. (1997) Regimes of coalescence and separation in droplet collision. *J. Fluid. Mech.* **331**, 59-80.
- Ross C. S. (1948) Optical Properties of Glass from Alamogordo, New Mexico. *American Mineralogist*. **33**, 360-362.
- Cornell R. and Schwertmann U. (2003) *The Iron Oxides: Structure, Properties, Reactions, Occurrences and Uses (2nd Ed)*. Wiley-VCH GmbH and Co. KGaA.

Walter L. S. and Giutronich J. E. (1967) Vapor Fractionation of Silicate Melts at High Temperatures and Atmospheric Pressures. *Solar Energy*. **11**, 163-169.

8. Tables

Table 1

Table 2

Table 3

9. Figures

Figure 1. Secondary electron image of Object A1, an agglomeration of many spheroidal objects ranging from tens to hundreds of micrometers in diameter. The smaller spheroidal objects show varying degrees of incorporation into a larger host object. For the full set of sample images, see the Electronic Annex 1.

Figure 2. Optical microscope images showing typical aerodynamic morphologies with multiple, smaller, spheroidal objects fused to the surface of the larger host object. The smaller attached objects exhibit various stages of incorporation into the larger object, evidencing an active agglomeration process preserved by rapid cooling conditions.

Figure 3. Back-scattered electron images of samples A-E. Each image shows one or more interfaces where small, spheroidal objects are attached to a larger host object. The interfaces are consistently highlighted as a high-Z (bright) boundary. Note that the brightness and contrast settings were chosen to highlight features within the individual images, and do not translate between the sample images. Top panes (left to right): Object A1; Objects B1, B2, and B3; Objects D1 and D2; Bottom panes (left to right): Object C3; Objects C1 and C2; Object E1.

Figure 4. (A) X-ray intensity maps of aluminum, calcium, iron, and sodium for Object C1 (right attached object) and C2 (left attached object). The relative concentration for each element is shown as an intensity map, where dark blue is low concentration and yellows/reds are the highest concentrations. The interfaces are enriched in Fe and Ca, while Al is depleted. The Ca map shows that the observed bright interface in BSE (see Fig. 3) is a continuous layer, circumscribing the attached object. The Na map of Object C1 shows enrichment of Na at the interface and edge. (B) X-ray intensity map of Na for Object E1, showing uniform enrichment of Na around the periphery of the attached object, along with semi-quantitative EDS profiles of Na and K along the red line in the Na map in the direction of the arrow.

Figure 5. EPMA line scan within Object C1. In panel (A) a BSE image of the object the BSE image indicates the approximate location of the scan with a yellow line. The line scan comprises 1 micrometer diameter points spaced approximately 1.5 micrometers apart. Data were collected for oxides of (B) Fe, (C) Ca, (D) Si, (E) Al, and (F) Ti. The gray data points illustrate the compositional variation of major elements from the edge of the object towards the center, while the blue data points show the variation of major elements across the interface. The uncertainties are 1σ , based on counting statistics. Enrichments of Fe and Ca are apparent at the interface and at the edge, while Al is depleted at the interface and the edge. The behavior of Ti shows no resolvable pattern at the sample edge, but a region of chemical depletion approximately co-located with the Fe interface maximum is seen. The concentration of SiO_2 remains relatively constant at the edge and the interface, changing by <6% of the maximum value.

Figure 6. (A) Major element oxide plot of CaO and Al₂O₃ taken from quantitative WDS data collected across the agglomerated objects, and across the interface where they fused to larger objects. The interior data represent 903 data points taken in the interior of the agglomerated objects; the gray shaded region shows the compositional range of the entire dataset. The interface points, indicated in blue, represent data points taken at the Al₂O₃ trough of relative depletion in concentration. The interface data points are depleted in Al₂O₃ for all samples, and the CaO content at the interface is enriched in 8 of the 9 samples. (B) Major element oxide plot of FeO and TiO₂ from the same dataset, with the shaded region depicting the range of the interior dataset. Here, FeO is observed to be enriched at the interface with a corresponding depletion of TiO₂ at 6 of the 9 sample interfaces.

Figure 7. (A) NanoSIMS ion images of ⁵⁴Fe/³⁰Si, ⁴⁴Ca/³⁰Si, ²³⁵U/³⁰Si, and ²³⁵U/²³⁸U are shown to the right of a BSE image for the interface of Object C1. The ²³⁵U/³⁰Si ion image is superimposed over the BSE image (red box), at the location the ion images were acquired. ⁵⁴Fe/³⁰Si, ⁴⁴Ca/³⁰Si, and ²³⁵U/³⁰Si images reveal the variation of these elements across the interface, assuming the ³⁰Si concentration is relatively constant (<10% variation in ³⁰Si signal intensity observed, consistent with acquired EDS data). The enrichment of ⁵⁴Fe, ⁴⁴Ca, and ²³⁵U at the interface, in combination with the ²³⁵U/²³⁸U image, show that U at the interface is predominantly ²³⁵U (>80%). This is clearly seen in panel B, which shows the isotope ratio data from a traverse across the interface along the location of the white arrow in the ⁵⁴Fe/³⁰Si image. The Fe, Ca, and U maxima all display quasi-Gaussian shapes. At the mid-point of the traverse, the ²³⁵U/²³⁸U plot yields an enrichment of $88.6 \pm 0.4\%$ ²³⁵U. This pattern of uranium enrichment co-located with Fe and Ca enrichment as well as U isotope enrichment was observed at nearly every analyzed interface.

Figure 8. ⁵⁴Fe/³⁰Si, ⁴⁴Ca/³⁰Si, and ²³⁵U/³⁰Si ratios normalized to their respective maximum values are overlain to illustrate the relative spatial distribution of Fe, Ca, and U across the interface of Object C1 with host sample C, showing the characteristic co-location of the Fe, Ca, and U enrichments.

Figure 9. BSE images from Objects B1 and B2 (left-most frames) shown with ²³⁵U/³⁰Si ion images of the interfaces. The middle frame shows the ²³⁵U/³⁰Si ion image of the interfaces, while isotope ratio variation along a line orthogonal to the interface is shown in the right-most frames. Corresponding data are provided in Table 3. Interface B1 shows the characteristic variation across the interface preserving local maxima and minima, while interface B2 shows an atypical pattern across the interface, where a region of high ²³⁵U/³⁰Si appears to have partially diffused into a region of low ²³⁵U/³⁰Si, preserving no distinct maximum at the interface. The bright white squares seen in the BSE images are an analytical artifact, where the carbon coating was removed during NanoSIMS analysis.

Figure 10. BSE images from Objects C1 (top left) and D2 (bottom left) relative to their larger host objects showing the degree of chemical heterogeneity in the samples. The contrast histogram of C1 is much narrower than that of host sample C, while the contrast histogram of D2 is approximately the same as host sample D, showing that Object C1 is comparatively more homogeneous than Object D2 when compared to their respective host objects. Note that while the contrast variation plots of C1 and D2 appear similar, these BSE images were taken under different contrast/brightness conditions and cannot be compared in an absolute sense.

Figure 11. (A) BSE image of the approximate location of the ion image acquired for Object B3, where Object B3 is in the top left of the image, and host sample B is in the bottom right (image collected from the far left interface as seen in Fig. 3). (B) ²³⁵U/³⁰Si ratio ion image, showing that a layer of isotopically distinct ²³⁵U at the boundary is abutted on either side by regions of relative ²³⁵U depletion. The white outline indicates the location of a corresponding high ⁵⁴Fe/³⁰Si region adjacent to the high ²³⁵U/³⁰Si region. (C) The corresponding ⁵⁴Fe/³⁰Si ratio image, showing the layer of Fe defining the boundary in the BSE image is offset from the high ²³⁵U region, and is instead co-located with a local region of relative ²³⁵U depletion.

Summary of figures and tables for Electronic Annexes 1-5

Figures:

Figure EA1a: BSE image of Object A1 fused to Sample A.

Figure EA1b: BSE image of Sample A, featuring a silica-rich inclusion in the center-right of the image.

Figure EA2: BSE image of Objects B1, B2, and B3 and the larger host object to which they are fused.

Figure EA3: BSE image of Objects C1, C2, and C3 and the larger host object to which they are fused.

Figure EA4: BSE image of Objects D1 and D2, and the larger host object to which they are fused.

Figure EA5: BSE image of Objects E1 and E2, and the larger host object to which they are fused.

Figure EA6: BSE images of two characteristic, mm-scale environmental grains proximate to ground zero of this nuclear test.

Figure EA7: EDS maps for Al, Ca, Fe, and Na of Object A1 are presented, as no EPMA maps were acquired for this object.

Figure EA8: WDS maps for Al, Ca, Fe, and Na of Objects B1, B2, and B3 are presented.

Figure EA9: WDS maps for Al, Ca, Fe, and Na of Objects C1 and C2 are presented.

Figure EA10: WDS maps for Al, Ca, Fe, and Na of Object C3 are presented.

Figure EA11: WDS maps for Al, Ca, Fe, and Na of Objects D1 and D2 are presented.

Figure EA12: WDS maps for Al, Ca, Fe, and Na of Object E1 are presented. The Na map clearly shows a layer of Na surrounding the smaller attached objects.

Figure EA13: WDS maps for Al, Ca, Fe, and Na of Object E2 are presented.

Figure EA14: Isotope ratio images of $^{56}\text{Fe}/^{30}\text{Si}$, $^{44}\text{Ca}/^{30}\text{Si}$, $^{235}\text{U}/^{30}\text{Si}$, and $^{235}\text{U}/^{238}\text{U}$ at the interface of Object A1 (left panes) and isotope ratio profiles (right panes) along a line normal to and across the interface (bottom left to top right).

Figure EA15: Isotope ratio images of $^{54}\text{Fe}/^{30}\text{Si}$, $^{44}\text{Ca}/^{30}\text{Si}$, $^{235}\text{U}/^{30}\text{Si}$, and $^{235}\text{U}/^{238}\text{U}$ at the interface of Object B1 (left panes) and isotope ratio profiles (right panes) along a line normal to and across the interface (from bottom left to top right).

Figure EA16: Isotope ratio images of $^{54}\text{Fe}/^{30}\text{Si}$, $^{44}\text{Ca}/^{30}\text{Si}$, $^{235}\text{U}/^{30}\text{Si}$, and $^{235}\text{U}/^{238}\text{U}$ at the interface of Object B2 (left panes) and isotope ratio profiles (right panes) along a line normal to and across the interface (bottom left to top right).

Figure EA17: Isotope ratio images of $^{54}\text{Fe}/^{30}\text{Si}$, $^{44}\text{Ca}/^{30}\text{Si}$, $^{235}\text{U}/^{30}\text{Si}$, and $^{235}\text{U}/^{238}\text{U}$ at the interface of Object B3 (left panes) and isotope ratio profiles (right panes) along a line normal to and across the interface (top left to bottom right).

Figure EA18: Isotope ratio images of $^{54}\text{Fe}/^{30}\text{Si}$, $^{44}\text{Ca}/^{30}\text{Si}$, $^{235}\text{U}/^{30}\text{Si}$, and $^{235}\text{U}/^{238}\text{U}$ at the interface of Object C1 (left panes) and isotope ratio profiles (right panes) along a line normal to and across the interface (bottom right to top left).

Figure EA19: Isotope ratio images of $^{54}\text{Fe}/^{30}\text{Si}$, $^{44}\text{Ca}/^{30}\text{Si}$, $^{235}\text{U}/^{30}\text{Si}$, and $^{235}\text{U}/^{238}\text{U}$ at the interface of Object C2 (left panes) and isotope ratio profiles (right panes) along a line normal to and across the interface (top left to bottom right).

Figure EA20: Isotope ratio images of $^{54}\text{Fe}/^{30}\text{Si}$, $^{44}\text{Ca}/^{30}\text{Si}$, $^{235}\text{U}/^{30}\text{Si}$, and $^{235}\text{U}/^{238}\text{U}$ at the interface of Object D1 (left panes) and isotope ratio profiles (right panes) along a line normal to and across the interface (top to bottom of the image).

Figure EA21: Isotope ratio images of $^{54}\text{Fe}/^{30}\text{Si}$, $^{44}\text{Ca}/^{30}\text{Si}$, $^{235}\text{U}/^{30}\text{Si}$, and $^{235}\text{U}/^{238}\text{U}$ at the interface of Object D2 (left panes) and isotope ratio profiles (right panes) along a line normal to and across the interface (top left to bottom right).

Figure EA22: Isotope ratio images of $^{54}\text{Fe}/^{30}\text{Si}$, $^{44}\text{Ca}/^{30}\text{Si}$, $^{235}\text{U}/^{30}\text{Si}$, and $^{235}\text{U}/^{238}\text{U}$ at the interface of Object E1 (left panes) and isotope ratio profiles (right panes) along a line normal to and across the interface (bottom left to top right).

Figure EA23: (a) EPMA analyses for Na_2O on homogenized Lake County obsidian glass for spot sizes ranging from 20 microns down to the focused probe diameter (<1 micron), showing a systematic decrease in concentration with increasing probe diameter. (b) EPMA analyses for K_2O using the same parameters, showing no discernible volatilization trend.

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Figure EA1a: BSE image of Object A1 and the larger host object to which it is fused. The plot on the right hand side shows the relative contrast variation within the larger host object (red) superimposed over the contrast variation of smaller fused Object A1 (gray). As seen from the plot, there is slightly more variation seen in the larger object, and there is a notable secondary peak at ~ 0.3 relative brightness, which is likely highlighting the dark, silica-rich inclusions in the BSE image, indicating heterogeneity not seen in Object A1.

Figure EA1b: BSE image of the host object of Sample A, featuring a silica-rich inclusion in the center-right of the image. The red arrow indicates the location and direction of an EDS line traverse that was acquired to qualitatively understand compositional variation across one of these features. The results from the line scan are shown in the right frame, for Si, Al, Fe, and Ca. Uncertainties are based solely on counting statistics.

Figure EA2: BSE image of Objects B1, B2, and B3 and the larger host object to which they are fused. The larger host object appears to show a larger range in contrast variation than the smaller attached spherules. However, this could be due to a systematic decrease in brightness towards the left side of the object, which may be due to topographical variation.

Figure EA3: BSE image of Objects C1, C2, and C3 and the larger host object to which they are fused. The contrast variation plot on the right shows Object C1 (gray) in comparison to the larger host. As seen in the plot, there is a much greater degree of contrast variation in the larger host object, indicating greater compositional heterogeneity.

Figure EA4: BSE image of Objects D1 and D2, and the larger host object to which they are fused. The plot on the right shows Object D1 and D2 (gray) in comparison to the larger host object, which shows a similar degree of compositional variation based on the contrast variation.

Figure EA5: BSE image of Object E1 and E2, and the larger host object to which they are fused. The plot on the right shows that attached Object E1 has a much narrower range of contrast variation relative to the larger attached object, indicative that the smaller spherule is considerably less heterogeneous compositionally.

Figure EA6: BSE images of two characteristic, mm-scale environmental grains proximate to ground zero of this nuclear test. In the left image, the darkest gray regions are quartz minerals, light gray is feldspar of varying composition, and the bright regions are high-Fe bearing minerals. In the right image, the central, bright minerals are identified as ilmenite.

Figure EA7: EDS maps for Al, Ca, Fe, and Na of Object A1 are presented, as no EPMA maps were acquired for this sample. The Fe, Ca, and Na maps show distinct enrichment around the perimeter, while Al shows characteristic depletion in the corresponding location.

Figure EA8: WDS maps for Al, Ca, Fe, and Na of Objects B1, B2, and B3 are presented. The Ca and Na maps show enrichment at interfaces, while Al shows characteristic depletion. Fe enrichment is not as distinct, given the lower count rate in mapping.

Figure EA9: WDS maps for Al, Ca, Fe, and Na of Objects C1 and C2 are presented. This figure is identical to Figure 4, but is presented here for completion of the EPMA map catalogue, and comparison to other supplemental figures.

Figure EA10: WDS maps for Al, Ca, Fe, and Na of Object C3 are presented. The major element maps follow the same trend of enrichments and depletions for the given elements, but has a notable enrichment in Na as compared to the larger host object.

Figure EA11: WDS maps for Al, Ca, Fe, and Na of Objects D1 and D2 are presented. As seen in the Ca map, there is a high degree of compositional variability, especially in the larger host object.

Figure EA12: WDS maps for Al, Ca, Fe, and Na of Object E1 are presented. The Na map clearly shows a layer of Na surrounding the smaller attached objects. Further, in the Ca map, it can be seen that there may be another attached object between the spherule and the host object.

EA1

Figure EA13: WDS maps for Al, Ca, Fe, and Na of Object E2 are presented. The Na map clearly shows a layer of Na surrounding the smaller attached object, and is incorporated into the larger host. The Ca map outlines another object adjacent to it, and also incorporated into the host.

Sample A1

Figure EA14: Isotope ratio images of $^{56}\text{Fe}/^{30}\text{Si}$, $^{44}\text{Ca}/^{30}\text{Si}$, $^{235}\text{U}/^{30}\text{Si}$, and $^{235}\text{U}/^{238}\text{U}$ at the interface of Object A1 (left panes) and isotope ratio profiles (right panes) along a line normal to and across the interface (bottom left to top right). It can clearly be seen that there is an enrichment of Fe and Ca at the interface (as seen in Figure EA7). The $^{235}\text{U}/^{30}\text{Si}$ image shows a depletion of U co-located with the Fe enrichment; however, there is a region of relatively high U located approximately 4 microns along the traverse. The $^{235}\text{U}/^{238}\text{U}$ does not show discernable variation, but does indicate a high level of isotopic enrichment of ^{235}U . At the very left, a BSE image is shown of the interface, with the $^{235}\text{U}/^{30}\text{Si}$ image superimposed at the location of the raster. **See Electronic Annex 5 for full NanoSIMS dataset for Figures EA14-22.**

Sample B1

Figure EA15: Isotope ratio images of $^{54}\text{Fe}/^{30}\text{Si}$, $^{44}\text{Ca}/^{30}\text{Si}$, $^{235}\text{U}/^{30}\text{Si}$, and $^{235}\text{U}/^{238}\text{U}$ at the interface of Object B1 (left panes) and isotope ratio profiles (right panes) along a line normal to and across the interface (from bottom left to top right). There is characteristic enrichment of Fe, Ca, and ^{235}U , all normalized to ^{30}Si . The $^{235}\text{U}/^{238}\text{U}$ oxide image is given here, as the oxide ion yield is substantially higher than the individual ions of ^{235}U and ^{238}U . There is a higher $^{235}\text{U}/^{238}\text{U}$ oxide ratio in one object with respect to the other, but no discernible increase in ratio at the interface itself.

Sample B2

Figure EA16: Isotope ratio images of $^{54}\text{Fe}/^{30}\text{Si}$, $^{44}\text{Ca}/^{30}\text{Si}$, $^{235}\text{U}/^{30}\text{Si}$, and $^{235}\text{U}/^{238}\text{U}$ at the interface of Object B2 (left panes) and isotope ratio profiles (right panes) along a line normal to and across the interface (bottom left to top right). While there is a characteristic enrichment of Fe and Ca at the interface, there is no indication of this pattern in ^{235}U at the interface. This interface is discussed in detail in the paper (Figure 9). Also of note, the $^{235}\text{U}/^{238}\text{U}$ oxide variation very clearly corresponds to the $^{235}\text{U}/^{30}\text{Si}$ ratio.

Sample B3

Figure EA17: Isotope ratio images of $^{54}\text{Fe}/^{30}\text{Si}$, $^{44}\text{Ca}/^{30}\text{Si}$, $^{235}\text{U}/^{30}\text{Si}$, and $^{235}\text{U}/^{238}\text{U}$ at the interface of Object B3 (left panes) and isotope ratio profiles (right panes) along a line normal to and across the interface (top left to bottom right). As also seen in Object A1, there is a region of depletion adjacent to a region of relative enrichment in the $^{235}\text{U}/^{30}\text{Si}$ image and profile. This interface is discussed in more detail in the paper (Figure 11). As in Figure EA17, the $^{235}\text{U}/^{238}\text{U}$ oxide variation very clearly corresponds to the $^{235}\text{U}/^{30}\text{Si}$ ratio.

Sample C1

Figure EA18: Isotope ratio images of $^{54}\text{Fe}/^{30}\text{Si}$, $^{44}\text{Ca}/^{30}\text{Si}$, $^{235}\text{U}/^{30}\text{Si}$, and $^{235}\text{U}/^{238}\text{U}$ at the interface of Object C1 (left panes) and isotope ratio profiles (right panes) along a line normal to and across the interface (bottom right to top left). This figure is identical to Figure 7 and is discussed in detail in the body of the paper. The figure is provided again here to complete the NanoSIMS ion image catalogue of samples and for comparison to other supplemental figures.

Sample C2

Figure EA19: Isotope ratio images of $^{54}\text{Fe}/^{30}\text{Si}$, $^{44}\text{Ca}/^{30}\text{Si}$, $^{235}\text{U}/^{30}\text{Si}$, and $^{235}\text{U}/^{238}\text{U}$ at the interface of Object C2 (left panes) and isotope ratio profiles (right panes) along a line normal to and across the interface (top left to bottom right). This interface is of particular interest given the distinct skewing of the isotope ratio profiles towards the larger host object. Further, the $^{44}\text{Ca}/^{30}\text{Si}$ ion ratio image and profile correspond with the high-Ca layer around a region of lower relative Ca concentration in the EPMA map seen in Figure EA9.

Sample D1

Figure EA20: Isotope ratio images of $^{54}\text{Fe}/^{30}\text{Si}$, $^{44}\text{Ca}/^{30}\text{Si}$, $^{235}\text{U}/^{30}\text{Si}$, and $^{235}\text{U}/^{238}\text{U}$ at the interface of Object D1 (left panes) and isotope ratio profiles (right panes) along a line normal to and across the interface (top to bottom of the image). This sample exemplifies characteristic profiles of every isotope ratio.

Sample D2

Figure EA21: Isotope ratio images of $^{54}\text{Fe}/^{30}\text{Si}$, $^{44}\text{Ca}/^{30}\text{Si}$, $^{235}\text{U}/^{30}\text{Si}$, and $^{235}\text{U}/^{238}\text{U}$ at the interface of Object D2 (left panes) and isotope ratio profiles (right panes) along a line normal to and across the interface (top left to bottom right). The $^{44}\text{Ca}/^{30}\text{Si}$ image shows what may be a low-Ca inclusion or void at the interface. The $^{235}\text{U}/^{30}\text{Si}$ ratio image also shows a less clear pattern of ^{235}U variation across the interface; however, this may be due to topography variation given its proximity to the large void seen in the BSE image (far left).

Sample E1

Figure EA22: Isotope ratio images of $^{54}\text{Fe}/^{30}\text{Si}$, $^{44}\text{Ca}/^{30}\text{Si}$, $^{235}\text{U}/^{30}\text{Si}$, and $^{235}\text{U}/^{238}\text{U}$ at the interface of Object E1 (left panes) and isotope ratio profiles (right panes) along a line normal to and across the interface (bottom left to top right). Of note at this interface, there is an abnormally wide profile of $^{235}\text{U}/^{30}\text{Si}$ enrichment that does not correspond to wider profiles of $^{54}\text{Fe}/^{30}\text{Si}$ or $^{44}\text{Ca}/^{30}\text{Si}$, although the regions of enrichment are generally co-located for all ratio profiles.

Figure EA23: (a) EPMA analyses for Na₂O on homogenized Lake County obsidian glass for spot sizes ranging from 20 microns down to the focused probe diameter (<<1 micron), showing a systematic decrease in concentration with increasing probe diameter. (b) EPMA analyses for K₂O using the same parameters, showing no discernible volatilization trend.

Table EA1.1:

Summary of analytical techniques applied to each of 11 fallout samples and soil samples collected proximate to ground zero.

Object ID	SEM	EDS	EPMA	NanoSIMS
A1	x	x		x
B1	x		x	x
B2	x		x	x
B3	x	x	x	x
C1	x	x	x	x
C2	x	x	x	x
C3	x	x	x	
D1	x	x		x
D2	x		x	x
E1	x	x	x	x
E2	x		x	
Soil	x		x	

Table EA1.2

Summary of U100 and U200 standards measurements as acquired by NanoSIMS

Sample ID	$^{235}\text{U}/^{238}\text{U}$	2-sigma	delta ^c	2-sigma	% deviation	2-sigma
<i>U100</i>	1.17×10^{-1}	0.02×10^{-1}	0.03×10^{-1}	0.02×10^{-1}	2.18	1.36
<i>U100</i>	1.15×10^{-1}	0.01×10^{-1}	0.01×10^{-1}	0.02×10^{-1}	0.53	1.31
<i>U100</i>	1.14×10^{-1}	0.04×10^{-1}	0.01×10^{-1}	0.04×10^{-1}	0.29	3.11
<i>U100</i>	1.15×10^{-1}	0.01×10^{-1}	0.01×10^{-1}	0.01×10^{-1}	0.99	0.20
<i>U100</i>	1.16×10^{-1}	0.01×10^{-1}	0.02×10^{-1}	0.01×10^{-1}	1.46	0.25
<i>U200</i>	2.43×10^{-1}	0.03×10^{-1}	0.08×10^{-1}	0.03×10^{-1}	3.37	1.23
<i>U200</i>	2.48×10^{-1}	0.03×10^{-1}	0.03×10^{-1}	0.03×10^{-1}	1.34	1.19
<i>U200</i>	2.46×10^{-1}	0.03×10^{-1}	0.05×10^{-1}	0.03×10^{-1}	1.93	1.28
^a U100 reference value	1.14×10^{-1}	0.03×10^{-1}				
^b U200 reference value	0.251258616	0.01×10^{-1}				

^aThe U100 standard used for this study was a glass matrix standard manufactured in-house and doped with ~10% ^{235}U isotopic composition. The reference value was determined in-house using a NuPlasma multi-collector inductively coupled plasma mass spectrometer.

^bThe CRM U200 standard was a U_3O_8 particle standard enriched to approximately 20% ^{235}U isotopic composition (Certificate of Analysis, 2008).

^cDelta is the difference between the measured value and the reference value