

# Isotopic Fingerprinting of the World's First Nuclear Device Using Post-Detonation Materials

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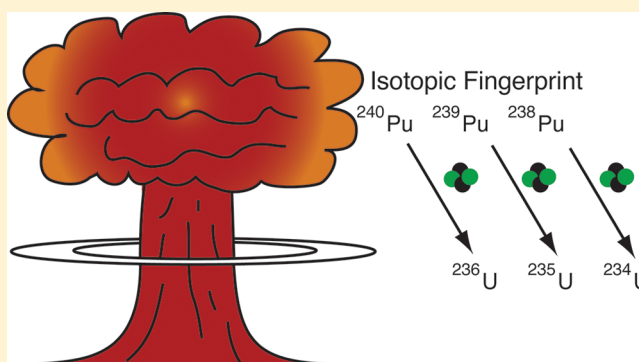
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## S Supporting Information

**ABSTRACT:** In the event of a rogue nuclear attack or interception of illicit nuclear materials, timely forensic investigations are critical for accurate source attribution. Uranium (U) and plutonium (Pu) isotopic ratios of intercepted materials or postdetonation samples are, perhaps, the most valuable evidence in modern nuclear forensics. These ratios simultaneously provide information regarding the material's "age" (i.e., time elapsed since last purification), actinide concentrations, and relevant isotopic ratios/enrichment values. Consequently, these isotope signatures are invaluable in determining the origin, processing history, and intended purpose of any nuclear material. Here we show, for the first time, that it is feasible to determine the U and Pu isotopic compositions of historic nuclear devices from their postdetonation materials utilizing in situ U isotopic measurements.

The U isotopic compositions of trinitite glass, produced subsequent to the world's first atomic explosion, indicate two sources: the device's tamper, composed of natural U that underwent fission during detonation, and natural U from the geological background. Enrichments in  $^{234,235,236}\text{U}$  reflect the in situ decay of  $^{238,239,240}\text{Pu}$ , the fuel used in the device. Time-integrated U isotopic modeling yields "supergrade" compositions, where  $^{240}\text{Pu}/^{239}\text{Pu} \approx 0.01\text{--}0.03$  and  $^{238}\text{Pu}/^{239}\text{Pu} \approx 0.00011\text{--}0.00017$ , which are consistent with the Pu originating from the Hanford reactor.<sup>1</sup> Spatially resolved U isotopic data of postdetonation debris reveal important details of the device in a relatively short time frame (hours). This capacity serves as an important deterrent to future nuclear threats and/or terrorist activities and is critical for source attribution and international security.



## INTRODUCTION

In the event of a nuclear attack by a rogue or nonstate actor, timely forensic investigations of postdetonation materials are needed to determine the elemental and isotopic compositions of the device and associated components. Ideally, once the chemical and isotopic signatures of a device are reconstructed, source attribution can be made quickly and accurately. Deciphering the chemical composition of a nuclear device from postdetonation materials in a relatively rapid manner will also serve as a strong deterrent to nuclear terrorism. Complicating factors include the inherent heterogeneity of the materials present at ground zero and possible overlapping chemical and isotopic signatures of the natural and anthropogenic (device) components. Moreover, traditional investigative methods for postdetonation are time-consuming,<sup>2–4</sup> and those involving bulk sample digestion followed by chemical separation tend to homogenize (average) the chemical and isotopic signatures. Hence, here we use emerging techniques to provide relatively rapid, spatially resolved isotopic data on postdetonation materials, which document the inherent isotopic variability present within individual samples. A first step in developing these techniques is to examine postdetona-

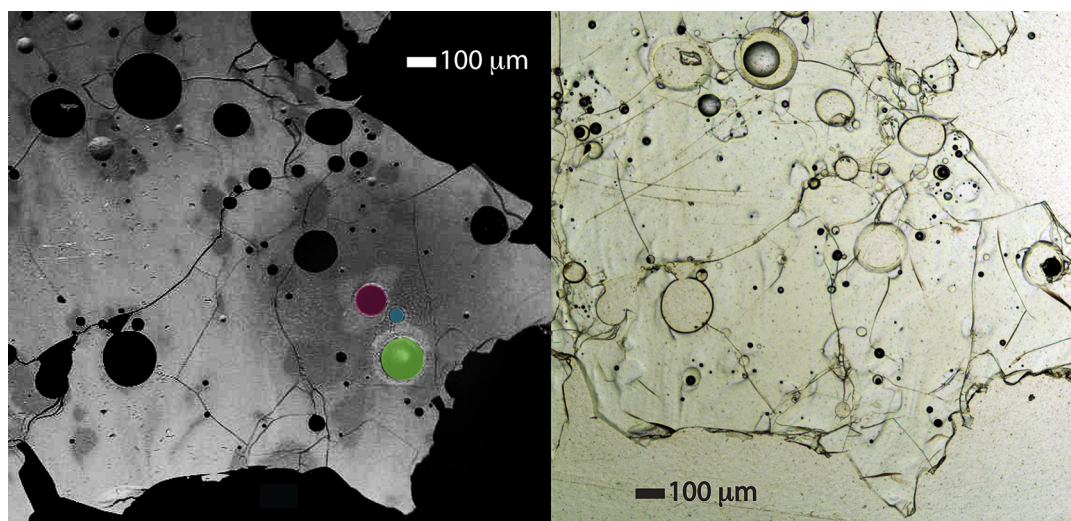
tion materials from historic test sites, as the nature of the device components employed are relatively well-documented. Hence, these materials provide a means to verify any results gained from their forensic analysis.

Green-glassy materials referred to as trinitite<sup>5</sup> are the postdetonation products from the first atomic weapon test, Trinity. Trinitite, which is the only postdetonation material commercially available, is ideally suited to establish non-classified nuclear forensics techniques. The Trinity nuclear test was conducted on the White Sands Proving Grounds (south of Alamogordo, NM) and took place on July 16, 1945 at 5:29:45 a.m. and ushered in the "Nuclear Age." The implosion-type device consisted of a Pu core, surrounded by a tamper constructed of natural U.<sup>6</sup> Prior to detonation, the bomb was hoisted to a height of 30.5 m upon a steel tower. The detonation produced a  $\sim 8430$  K, 21 kiloton explosion, and a 15–21 km high mushroom cloud,<sup>5</sup> which consumed the test site, blast tower, and surrounding arkosic sand. Therefore,

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**Figure 1.** A backscatter electron image and a plane-polarized photomicrograph of trinitite glass with laser pits. The green circle represents the diameter used for U isotopic analysis. The blue and red circles represent the diameters employed for trace-element and Pb isotopic analyses, respectively. Trace-element and Pb isotopic data are to be reported in future publications.

trinitite glass records the isotopic signatures of the device, blast tower, and natural signatures of the desert sand.

The foremost goal in postdetonation nuclear forensics is to precisely and accurately determine the isotopic composition of heavy elements (i.e., Pb, Pu, U) used in a device. These elements provide the best evidence for determining the region that produced the nuclear material since their isotopic compositions are dependent on the type of fuel, enrichment cycle, and ore(s) used.<sup>7,8</sup> This study reports the first robust isotopic investigation of trinitite glass and of postnuclear detonation materials available to the public. Specifically, we utilize U isotopic compositions for elucidating aspects of the design of the world's first nuclear device, including the fissile material used to fuel it.

**Uranium Isotope Systematics.** In the absence of U fission during detonation, the U isotope systematics in trinitite should reflect mixing of U from the tamper and the desert sand, which both had “natural” U isotopic compositions [ $^{235}\text{U}/^{238}\text{U} = 0.007256 \pm 0.0000002$  ( $2\sigma$ )<sup>9</sup>] and are therefore isotopically unresolvable. However, evidence from gamma spectroscopy shows that  $^{235}\text{U}$  present in the tamper did fission, and fission product ratios [ $^{155}\text{Eu}/^{137}\text{Cs} = 0.012 \pm 0.006$  and  $^{90}\text{Sr}/^{137}\text{Cs} = 2.15 \pm 0.02$  ( $1\sigma$ )] reflect mixing between  $^{235}\text{U}$  and  $^{239}\text{Pu}$  fission products.<sup>4,10</sup> Therefore, the postfission U signature should be evidenced by a marked depletion in  $^{235}\text{U}$  and enrichment in  $^{236}\text{U}$  produced by neutron capture by unfissioned  $^{235}\text{U}$ . Supergrade Pu ( $^{240}\text{Pu}/^{239}\text{Pu}$  of 0.0130–0.0176<sup>3,8</sup>) was used in the device and consisted of 4 isotopes:  $^{238}\text{Pu}$ ,  $^{239}\text{Pu}$ ,  $^{240}\text{Pu}$ , and  $^{241}\text{Pu}$ .  $^{238}\text{Pu}$  ( $t_{1/2} = 87.7$  y),  $^{239}\text{Pu}$  ( $t_{1/2} = 24110$  y), and  $^{240}\text{Pu}$  ( $t_{1/2} = 6561$  y) decay via  $\alpha$  emission into  $^{234}\text{U}$ ,  $^{235}\text{U}$ , and  $^{236}\text{U}$ , respectively.  $^{241}\text{Pu}$  decays into  $^{241}\text{Am}$  via  $\beta^-$  ( $t_{1/2} = 14.3$  y). All of the half-lives used in the modeling results reported here are from the following source: <http://www.nndc.bnl.gov/chart/chartNuc.jsp>. As such, the U isotopic composition of historic postdetonation materials involving a Pu device (i.e., trinitite) is inextricably linked with the isotopic composition of the Pu employed, as unfissioned Pu is entrained in the debris. Thus, measurement of the U isotopic compositions in trinitite at high spatial resolution (scale of tens of micrometers) should yield the signatures from the

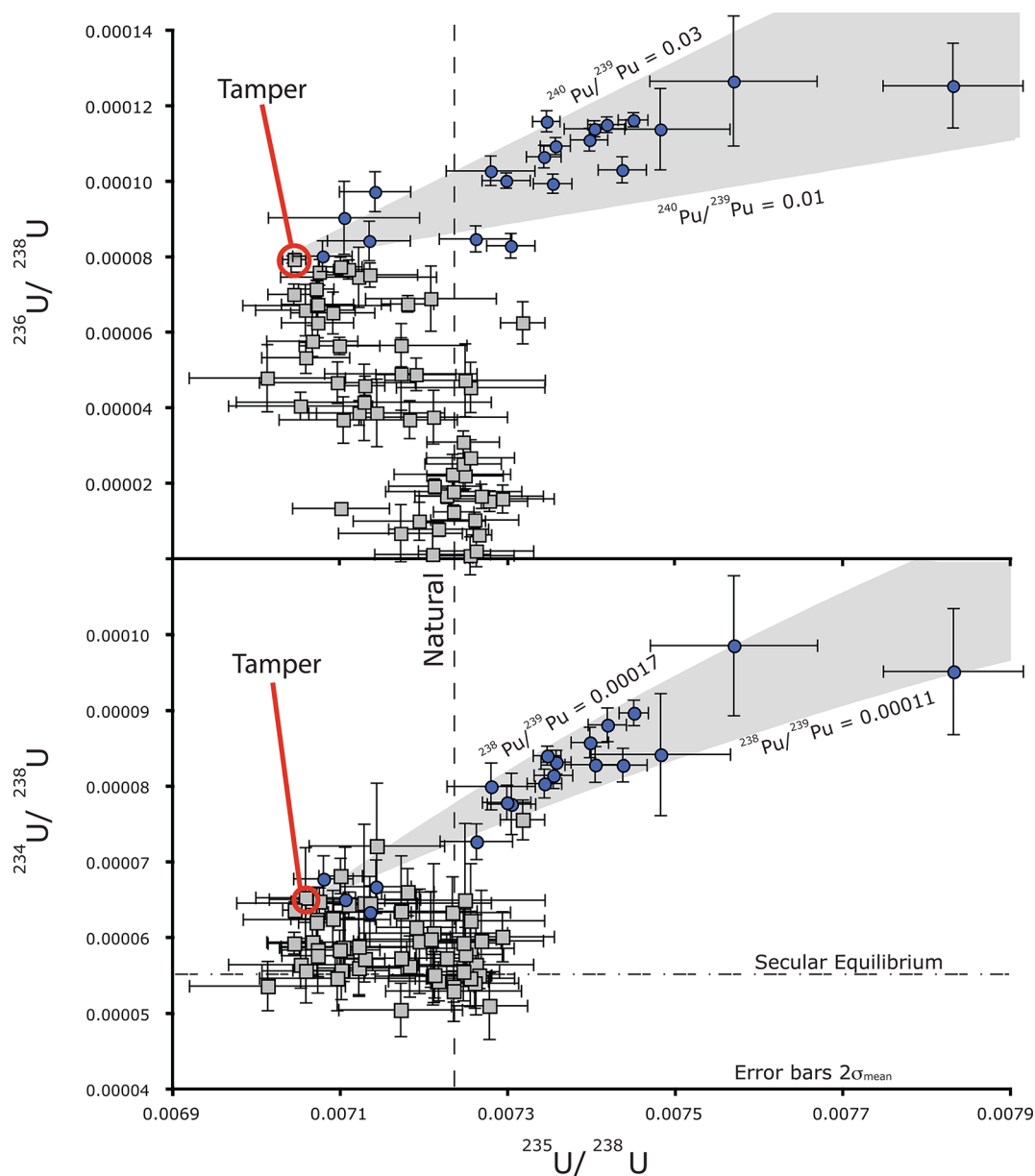
device, natural U, and from the in situ decay of Pu over the 67 years since the Trinity test.

## METHODS

The U isotopic compositions of individual points ( $n = 75$ ) in 12 samples of trinitite glass were measured in situ by laser ablation-multicollector-inductively coupled plasma-mass spectrometry (LA-MC-ICP-MS) on polished thin sections (60–100  $\mu\text{m}$ ). On the basis of the activity of  $^{152}\text{Eu}$  obtained by gamma spectroscopy, the samples investigated here yield calculated distances away from ground zero of 51–76  $\text{m}^4$ ; however, the latter are associated with relative uncertainties that range between  $\sim 1\%$  and  $\sim 20\%$  (average = 8%;  $1\sigma$  level), which restrict to some degree their interpretive significance. Uranium isotopic measurements were performed using an ESI New Wave 193 Excimer laser ablation system (NWR193) coupled to a Nu Plasma II Multi-Collector ICP-MS. Analyses employed spot sizes of 150  $\mu\text{m}$  with a fluence of 12  $\text{J}/\text{cm}^2$  and a repetition rate of 6 Hz (Figure 1). On-peak backgrounds were collected for 45 s with the laser on and shuttered. Ablation signals were collected for 40–80s, resulting in a total analysis time of <2 min. Ion beams of all four U isotopes were collected simultaneously with  $^{238}\text{U}$  measured in a Faraday cup, whereas ion signals for  $^{234}\text{U}$ ,  $^{235}\text{U}$ ,  $^{236}\text{U}$  were recorded using ion counters. Correction for instrumental mass bias was performed using a standard-sample bracketing method with a NIST SRM 610 glass wafer as the external standard, the exponential fractionation law, and U isotope values from Barnes et al., 1973.<sup>11</sup> Tables containing data for trinitite, NIST SRM 612 treated as an “unknown”, three terrestrial zircon standards, and additional analytical methods are located in the Supporting Information.

## RESULTS AND DISCUSSION

The plot of  $^{236}\text{U}/^{238}\text{U}$  versus  $^{235}\text{U}/^{238}\text{U}$  exhibits two groups of data (Figure 2). The first group is identified by enrichment in  $^{236}\text{U}$  and depletion in  $^{235}\text{U}$  and can be attributed to fission of the natural U present within the tamper of the device. The data plotting toward the isotope value for natural U can be attributed to the dilution by randomly distributed U-bearing



**Figure 2.** Illustrates the U isotopic compositions for trinitite. Natural values calculated from Hiess et al.<sup>9</sup> Gray ■ represent non-Pu-influenced U isotopic compositions resulting from mixing between the tamper and natural U. Blue ● reflect U isotopic compositions interpreted to be influenced by the in-growth of Pu.

minerals (e.g., zircon, apatite, and monazite) present at trace amounts within the arkosic sand. The second group of data in the  $^{236}\text{U}/^{238}\text{U}$  versus  $^{235}\text{U}/^{238}\text{U}$  diagram is defined by significant enrichments in both  $^{236}\text{U}$  and  $^{235}\text{U}$  and can be modeled by the in situ decay of  $^{240}\text{Pu}$  and  $^{239}\text{Pu}$ , respectively, contained locally within trinitite. A model of present-day U isotopic compositions that are a result of the decay of Pu, since the formation of trinitite can be made based on the following input parameters and equations: (1) an initial U isotopic composition at the time of trinitite formation, (2) the decay equations for each Pu isotope, (3) a time ( $t$ ) of 67 y, and (4) stipulating a  $^{239}\text{Pu}/^{238}\text{U}$  ratio.

$$^{235}\text{U}/^{238}\text{U}(\text{present}) = ^{235}\text{U}/^{238}\text{U}(\text{initial}) + ^{239}\text{Pu}/^{238}\text{U}(e^{\lambda_{239}\text{Pu}t} - 1) \quad (1)$$

$$^{236}\text{U}/^{238}\text{U}(\text{present}) = ^{236}\text{U}/^{238}\text{U}(\text{initial}) + ^{239}\text{Pu}/^{238}\text{U} \times ^{240}\text{Pu}/^{239}\text{Pu} \times (e^{\lambda_{240}\text{Pu}t} - 1) \quad (2)$$

$$^{234}\text{U}/^{238}\text{U}(\text{present}) = ^{234}\text{U}/^{238}\text{U}(\text{initial}) + ^{239}\text{Pu}/^{238}\text{U} \times ^{238}\text{Pu}/^{239}\text{Pu} \times (e^{\lambda_{238}\text{Pu}t} - 1) \quad (3)$$

For this study, it is assumed that the initial U isotopic composition in Pu-bearing trinitite is that of the postfission tamper (Figure 2). Therefore, the initial U isotopic composition of Pu-bearing trinitite can be represented by the trinitite with the most enriched  $^{236}\text{U}$  and depleted  $^{235}\text{U}$  [ $^{235}\text{U}/^{238}\text{U} = 0.00704 \pm 0.00001$ ,  $^{236}\text{U}/^{238}\text{U} = 0.000079 \pm 0.000002$ , and  $^{234}\text{U}/^{238}\text{U} = 0.000064 \pm 0.0000001$  ( $2\sigma_{\text{mean}}$ )],

which reflects the tamper composition least diluted with natural U. This model yields a  $^{240}\text{Pu}/^{239}\text{Pu}$  composition of 0.01–0.03 and a maximum  $^{239}\text{Pu}/^{238}\text{U}$  ratio of 0.42 for trinitite, which is in agreement with previous measurements of Pu<sup>3,8,12</sup> and confirms the “super-grade” classification of the Pu used in the device.

Similarly, there are two groups of data shown in the plot of  $^{234}\text{U}/^{238}\text{U}$  versus  $^{235}\text{U}/^{238}\text{U}$  (Figure 2). The first group is characterized by depleted  $^{235}\text{U}/^{238}\text{U}$  values and slightly enriched  $^{234}\text{U}/^{238}\text{U}$  ratios (above secular equilibrium). The second group contains enriched  $^{235}\text{U}/^{238}\text{U}$  and  $^{234}\text{U}/^{238}\text{U}$  values that can be modeled by the presence of Pu. While the presence of  $^{240}\text{Pu}$  is seen as a contaminant in nuclear weapons because it undergoes spontaneous fission (possibly leading to early detonation and a reduction of the overall yield<sup>6</sup>),  $^{238}\text{Pu}$  was not monitored in the production of the device's core. Plutonium-238 is produced during the nuclear fuel cycle or during nuclear detonation. Due to the short irradiation times used to create the Pu<sup>6</sup> and the small time interval involved during detonation,  $^{238}\text{Pu}$  would have been present in trinitite in trace amounts. The time-integrated U isotopic modeling yields a  $^{238}\text{Pu}/^{239}\text{Pu}$  ratio of 0.00011–0.00017 and represents the value in the unfissioned Pu from the device after detonation.

## CONCLUSIONS

In conclusion, the results reported here clearly demonstrate that the capability to obtain rapid, spatially sensitive U isotopic ratios is critical in the forensic analysis of postdetonation nuclear materials. The complexities in U isotopic ratios reported here by LA-MC-ICP-MS analysis, obtained in ~2 min/analysis, would be masked by analytical protocols based on traditional dissolution and chemical separation techniques of bulk samples. Although a significant number of individual laser analyses are required (as in this study) in order to formulate interpretations with a significant level of confidence, the approach adopted here is nonetheless still less time-consuming compared to bulk separation techniques; moreover, the latter tends to average (homogenize) the U isotopic composition for each sample and would not accurately reflect their large internal heterogeneity. Development of a “rapid” forensics tool for accurate isotopic fingerprinting of nuclear weapons is essential for source attribution and can serve as a strong deterrent against potential future aggressions and, consequently, increase international security.

## ASSOCIATED CONTENT

### Supporting Information

Additional information as noted in text. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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### Notes

The authors declare no competing financial interest.

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