

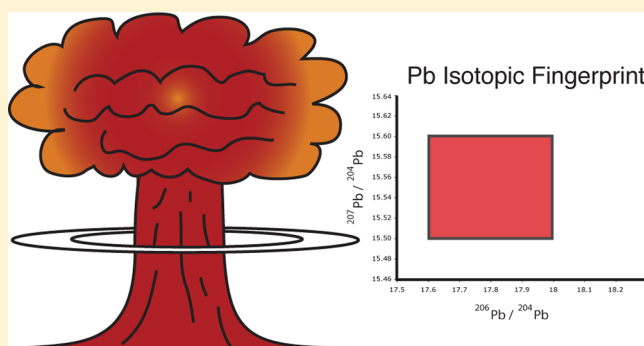
Lead Isotopic Composition of Trinitite Melt Glass: Evidence for the Presence of Canadian Industrial Lead in the First Atomic Weapon Test

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S Supporting Information

ABSTRACT: The Pb isotopic compositions for 51 spots of melt glass in 11 samples of trinitite have been determined by laser ablation multicollector inductively coupled plasma mass spectrometry (LA-MC-ICP-MS). Trinitite glass yields a large range of Pb isotopic compositions (i.e., $^{206}\text{Pb}/^{204}\text{Pb} = 17.08\text{--}19.04$), which reflect mixing between industrial Pb from materials used in the Trinity test and natural geologic components. Areas within trinitite melt glass containing high concentrations of both Cu and Pb, which are derived from the bomb and blast site-related components, were used for delineating the Pb isotopic composition corresponding to the anthropogenic Pb component. Comparison between the isotopic composition estimated here for the industrial Pb used in the Trinity test and those from known Pb deposits worldwide indicates close agreement with ore from the Buchans mine (Newfoundland, Canada). The Buchans mine was active during the time of the Trinity test and was operated by the American Smelting and Refining Company, which could have provided the Pb used in the test. The industrial Pb used in the Trinity test materials is not documented in the literature (or declassified) but could have been present in bricks, solder, pigs, or some other anthropogenic component related to the experiment.



Investigations of postdetonation nuclear materials (PDMs) are critical for security at both national and international levels. If a rogue group or terrorist organization acquires nuclear capability and uses a nuclear device in an act of terrorism, the composition of the device components and fuel are needed for accurate source attribution. To accomplish this goal, a multidisciplinary approach to understanding PDMs is necessary because these are extremely complex.^{1–7} The PDMs produced subsequent to the first atomic weapon test, Trinity, are available for public research. These PDMs, which are referred to collectively as “trinitite”, represent ideal samples to establish nuclear forensics techniques because most of the documentation associated with the Trinity test is now declassified, such as the Pu isotopic composition of the fuel employed. Hence, this available information provides a means to verify results obtained from nuclear forensic investigations.

The Trinity atomic weapon test took place on July 16, 1945, at 5:29:45 a.m. The test was conducted at the White Sands Proving Grounds, just south of Alamogordo, NM. The device, nicknamed “Gadget”, was fueled by supergrade Pu ($^{240}\text{Pu}/^{239}\text{Pu} = 0.01\text{--}0.03$).^{3,6–9} The center of Gadget contained a 2.5 cm diameter Be neutron initiator, surrounded by a 9.2 cm diameter Pu–Ga alloy core, a 22 cm diameter tamper constructed from natural U, and last a 22.9 cm diameter boron–plastic shell.¹⁰ The core of the device was surrounded by the implosion

assembly, which consisted of explosives and aluminum shells.¹⁰ The explosives used to initiate the nuclear detonation in the device were of RDX, trinitrotoluene (TNT), and Baratol, which is a mixture of TNT and $\text{Ba}(\text{NO}_3)_2$.¹⁰ Additionally, the device and surrounding equipment had an unknown amount of electronics, wiring, and other components. Prior to detonation, Gadget was hoisted onto a steel tower with a height of 30.5 m. Subsequent to ignition, a 21 kiloton explosion was produced, yielding a mushroom cloud with a height of 15.2–21.3 km and a temperature of $\sim 8430\text{ K}$.^{5,11}

The explosion consumed the blast tower, surrounding facilities, bomb components, and the surface of the desert sand. Consequently, these materials were mixed, and upon cooling formed the green blast melt “trinitite”. In general, trinitite is composed of two phases: melt glass and relict quartz grains.^{4,5,7} The melt glass contains the vast majority of radioactive elements and components from the device.^{4,7} Therefore, investigations into the melt glass of trinitite will yield the most informative (i.e., source attribution-related) forensic results. Trinitite is extremely heterogeneous at the micrometer scale,⁴ in terms of chemistry and petrology.^{5,7,8}

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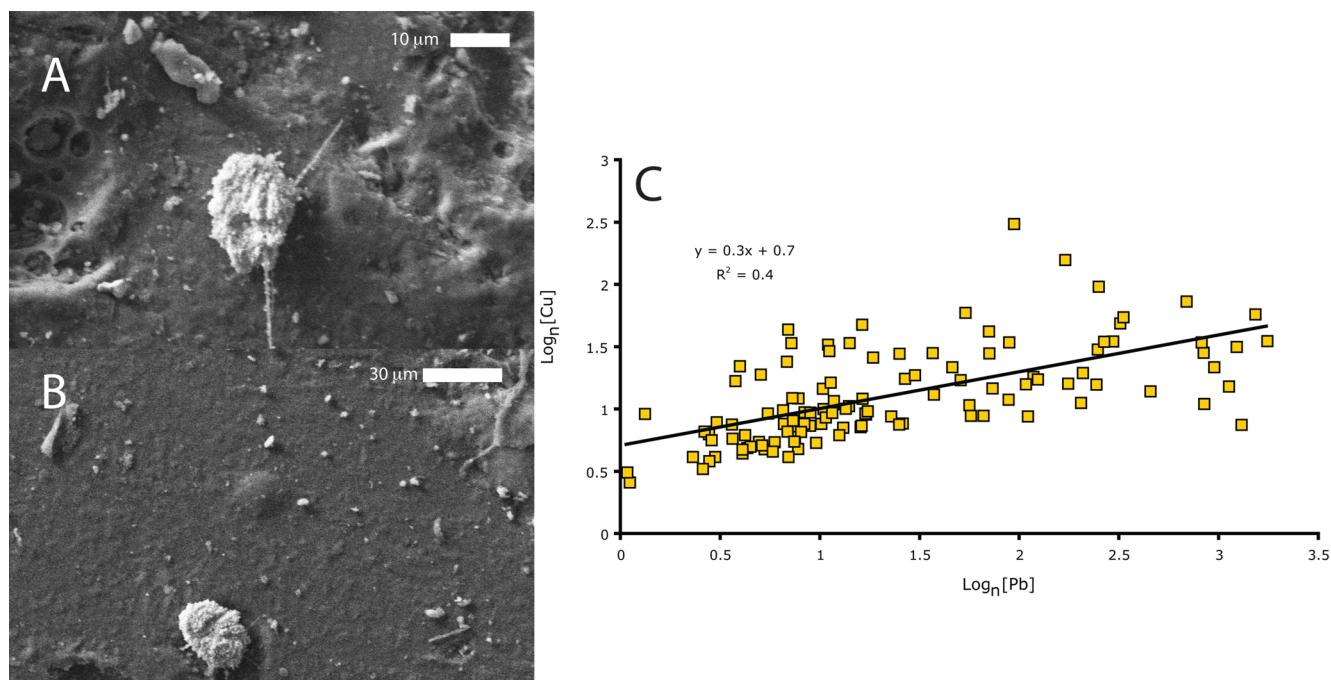


Figure 1. (A, B) Scanning electron microscope images of PbO inclusion on the surface of trinitite glass from Bellucci and Simonetti.¹⁶ (C) Log-normal covariate diagram of concentrations of Pb and Cu in trinitite melt glass from Bellucci et al.⁴.

Therefore, in situ analytical methods are preferred since specific areas of melt glass can be targeted at the tens to hundreds of micrometers scale; this facilitates delineating natural versus bomb components.^{3,4,7} In contrast, methods based on treatment of bulk samples may provide higher sensitivity in detecting radioactive isotopes in explosion debris; however, these are more likely to homogenize the chemical/isotopic compositions of end-member components and hence reduce the likelihood of successful forensic analysis.

The best forensic evidence to determine the provenance of a nuclear device lies in the isotopic composition of heavy metals (Pb, Pu, and U).^{3,7,8,12} Specifically, the isotopic composition of these elements reflects the ores, enrichment procedures, and fuel cycle used in creating the fuel and/or components for the device. In relation to the heavy metal Pb, it is composed of four isotopes: ²⁰⁸Pb, ²⁰⁷Pb, ²⁰⁶Pb, and ²⁰⁴Pb. ²⁰⁸Pb, ²⁰⁷Pb, and ²⁰⁶Pb are the decay products of the long-lived isotopes ²³²Th, ²³⁵U, and ²³⁸U, respectively. ²⁰⁴Pb is a primordial Pb isotope and not a progeny of U or Th parent isotopes. Therefore, the Pb isotopic composition of a given material is dependent on its initial Pb isotopic composition, its age, and its time-integrated Th–U–Pb history. Due to the large variations in the geochemical behavior of U, Th, and Pb, the Pb isotopic composition of rocks, minerals, and ores displays a significant natural variation. This variation can be used as an isotopic “fingerprint.” As such, this fingerprint can be used to link Pb ores and the industrial (anthropogenic) materials produced from them.^{13–15}

Lead has been observed as an oxide (PbO) inclusion on the surface of trinitite,¹⁶ and Pb abundances correlate positively with those for Cu in trinitite glass⁴ (Figure 1). However, the exact origin of industrial Pb in trinitite has yet to be determined because there is no documented use of Pb in Gadget or in the Trinity test.¹⁰ Furthermore, determining the Pb isotope composition of weapon components is critical since Pb could easily be employed as a tamper in a hypothetical improvised

device used in a terrorist attack.⁸ Thus, the main focus of this study is to determine the origin of the anthropogenic Pb component in trinitite melt glass based on the in situ, measured Pb isotopic composition of trinitite PDMs obtained by laser ablation multicollector inductively coupled plasma mass spectrometry (LA-MC-ICP-MS).

METHODS

Trinitite samples investigated here ($n = 11$) were purchased from Mineralogical Research Corp. (www.minresco.com) and have been well-characterized relative to their major and trace element chemical composition, γ radioactivity, radionuclide abundances, and U isotope composition.^{2–4,7,16} Prior to

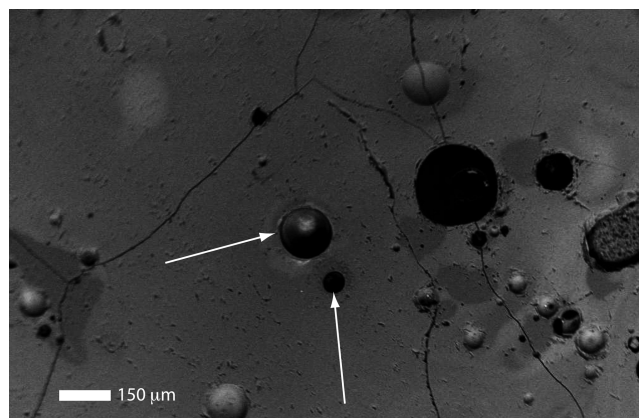


Figure 2. Backscatter electron image (BSE) of trinitite with laser pits (indicated with arrows). The large pit represents the location of a Pb isotopic analysis. The smaller laser pit represents a trace element analysis from Bellucci et al.⁴ All Pb isotopic analyses were conducted proximal to trace element analyses in regions that were homogeneous in terms of BSE images. Dark areas are relict quartz grains, while lighter areas represent trinitite melt glass.

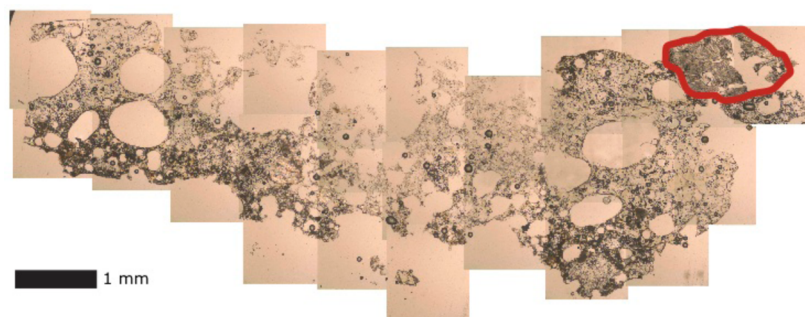


Figure 3. Plane-polarized photomicrograph of a thick section of trinitite exhibiting a pristine feldspar grain (outlined in red).

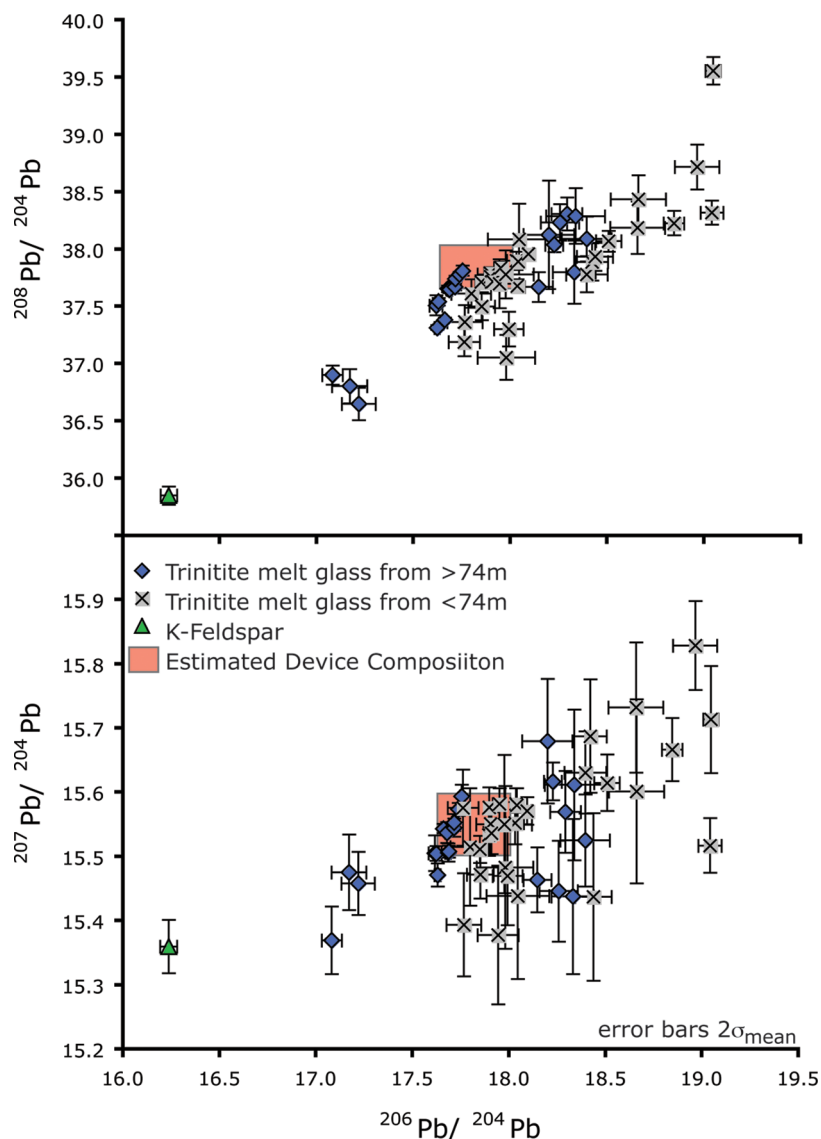


Figure 4. Pb–Pb isotope diagrams that show the compositions of a pristine feldspar grain, trinitite glass, and the estimated composition of the “Trinity” signature. Analyses are divided into two groups: (1) melt glass from samples that originate in samples $<74\text{ m}$ relative to ground zero and (2) melt glass from samples that originate $>74\text{ m}$ to ground zero. Calculated distances are based on ^{152}Eu activity and are taken from Bellucci et al.²

analysis, samples were cut and polished into sections with a thickness of $60\text{ }\mu\text{m}$. All Pb isotopic analyses were conducted on trinitite melt glass (Figure 2) and one pristine potassium feldspar crystal (Figure 3). Pristine crystalline phases are rare in trinitite; therefore, it was impossible to conduct additional analyses of the latter.

All in situ analyses were performed by use of an ESI New Wave Research 193 excimer laser system (NWR193) coupled to a Nu Plasma II MC-ICP-MS. Helium gas was used to transport ablated material from the laser ablation cell and was combined with Ar gas in a T-junction before the torch assembly. Typical gas flows, collector configurations, and laser

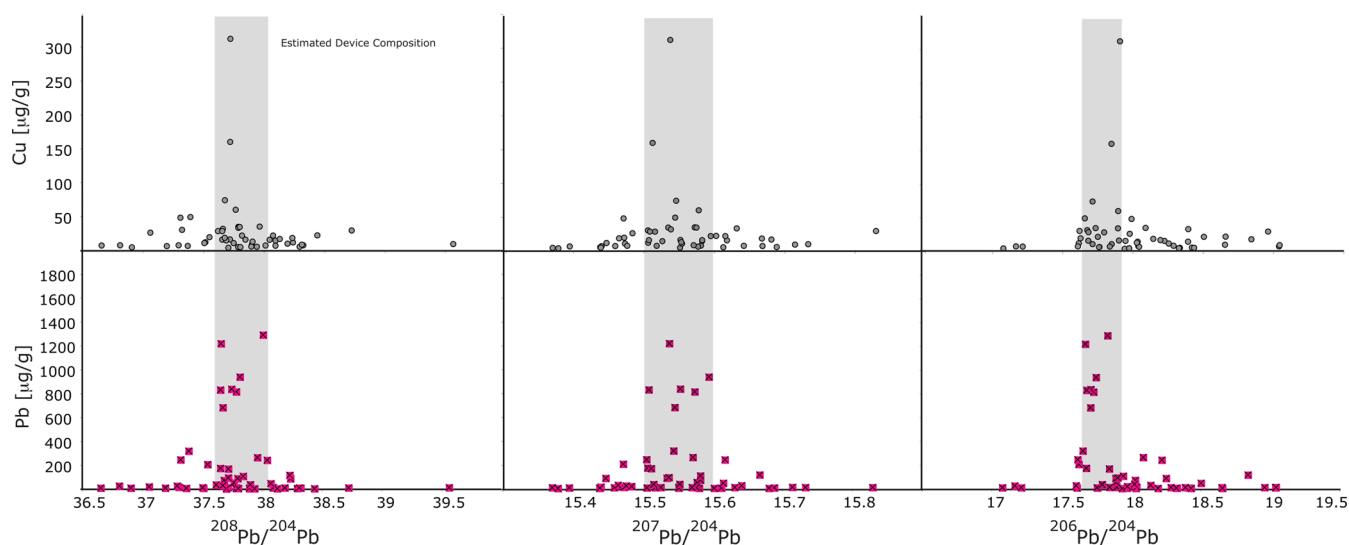


Figure 5. Pb isotopic compositions obtained here vs the concentrations of Pb and Cu in $\mu\text{g/g}$ from Bellucci et al.⁴ Gray bar represents the estimated composition of the industrial Pb present within anthropogenic materials employed at the Trinity test.

settings are listed in Supporting Information Table S1. The analytical procedure employed in this study is similar to that of Bellucci et al.¹⁷ and Kent.^{18,19} Background ion signal measurements were taken on peak for 45 s with the laser on and shuttered; laser ablation ion signals were subsequently collected for 40–80 s. The major isotopes of Pb (208, 207, and 206) were collected in Faraday cups, and mass 204 (Pb and Hg) and ²⁰²Hg ion signals were measured by use of discrete dynode secondary electron multipliers. The correction for the isobaric interference of ²⁰⁴Hg on ²⁰⁴Pb was conducted by using both the measured ²⁰⁰Hg ion signal and the natural Hg isotopic abundances²⁰ so as to calculate ²⁰⁴Hg. Instrumental mass bias was monitored and corrected for by using a standard-sample bracketing technique employing the NIST SRM 612 standard glass wafer. Measured Pb isotope ratios for the trinitite samples were corrected by use of the exponential law and NIST SRM 612 Pb isotopic values from Baker et al.²¹ The instrumental mass bias factor was determined on the basis of the ²⁰⁸Pb/²⁰⁶Pb ratio. Prior to the start of the analytical session, the preamplifier gains for all Faraday cups were calibrated relative to the axial Faraday cup. Faraday-ion counter gain calibrations were calculated by taking the ratio of the measured ^{20x}Pb/²⁰⁴Pb ($x = 8, 7, \text{ or } 6$) versus the expected ^{20x}Pb/²⁰⁴Pb. The expected ^{20x}Pb/²⁰⁴Pb ratios were calculated by use of the fractionation factor calculated from the measured ²⁰⁸Pb/²⁰⁶Pb in NIST 612. All measured Pb isotopic ratios were calculated with the Nu Plasma II time-resolved analysis (TRA) software, and fractionation/gain corrections were performed offline with Microsoft Excel.

RESULTS AND DISCUSSION

All Pb isotope results are listed in Supporting Information Table S2 and shown in Figure 4. The Pb isotopic composition of the pristine feldspar crystal is characterized by the least radiogenic values, whereas those for the trinitite melt glass exhibit a significant range (i.e., ²⁰⁶Pb/²⁰⁴Pb = 17.08–19.04). Interestingly, there are no extremely radiogenic Pb isotopic compositions (i.e., ²⁰⁶Pb/²⁰⁴Pb > 20), which could be attributed to Pb derived from the U ore used in the tamper. Hence, the lack of extremely radiogenic Pb isotopic compositions implies that the bomb-related, anthropogenic Pb in trinitite is derived

from a Pb-rich ore. Therefore, “unmasking” the Pb isotope fingerprint of the Trinity bomb-related components from the geological background is somewhat difficult given their significant overlap in values (Figure 4). However, Bellucci et al.⁴ reported that the concentrations of Pb and Cu are positively correlated within trinitite melt glass (Figure 1). Therefore, this relationship can be used to determine the Pb isotopic composition of the anthropogenic component; if it is assumed, of course, that both Pb and Cu are elements derived predominantly from the Gadget and/or blast site and not the geological background. Bulk sample trace element analysis of the original arkosic sand at the Trinity site yields a Pb concentration of $\sim 40 \mu\text{g/g}$ Pb, whereas the highest concentrations of Pb in trinitite are $>1500 \mu\text{g/g}$ Pb (Bellucci et al.⁴); therefore the areas of trinitite with the highest concentration of Pb likely reflect an anthropogenic signature. Based on this assumption and correlation between Pb and Cu concentrations, an estimate for the Pb isotopic composition of Trinity test-related (anthropogenic) component is ²⁰⁶Pb/²⁰⁴Pb = 17.6–18.0, ²⁰⁷Pb/²⁰⁴Pb = 15.5–15.6, and ²⁰⁸Pb/²⁰⁴Pb = 37.6–38.0 (Figure 5).

Within Pb–Pb isotope diagrams, mixing between distinct components results in linear trends (e.g., Figure 4). As such, the range of Pb isotopic ratios recorded by trinitite glass is likely a function of mixing between various U–Th–Pb-bearing phases within the arkosic sand present at ground zero. For example, the more radiogenic Pb component (i.e., ²⁰⁶Pb/²⁰⁴Pb > 18) may be attributed to Pb derived from U-bearing phases, such as zircon, monazite, and/or apatite. The presence of these phases has been identified on the basis of distinctive trace element signatures [e.g., Hf and Zr for zircon; U–Th and light rare earth elements (LREEs) for monazite and apatite] recorded within trinitite glass.⁴ The less radiogenic Pb component (i.e., ²⁰⁶Pb/²⁰⁴Pb < 17.6) may be attributed to a U-poor mineral, such as potassium feldspar (Figure 4).

A “model” age can be assigned to a Pb ore (or U-deficient mineral; e.g., potassium feldspar) based on its Pb isotopic composition since these are typically characterized by low U/Pb ratios, which results in negligible in-growth of radiogenic Pb. The calculated model age for a Pb ore is dependent on the Pb growth model parameters adopted/assumed.^{22–26} For example,

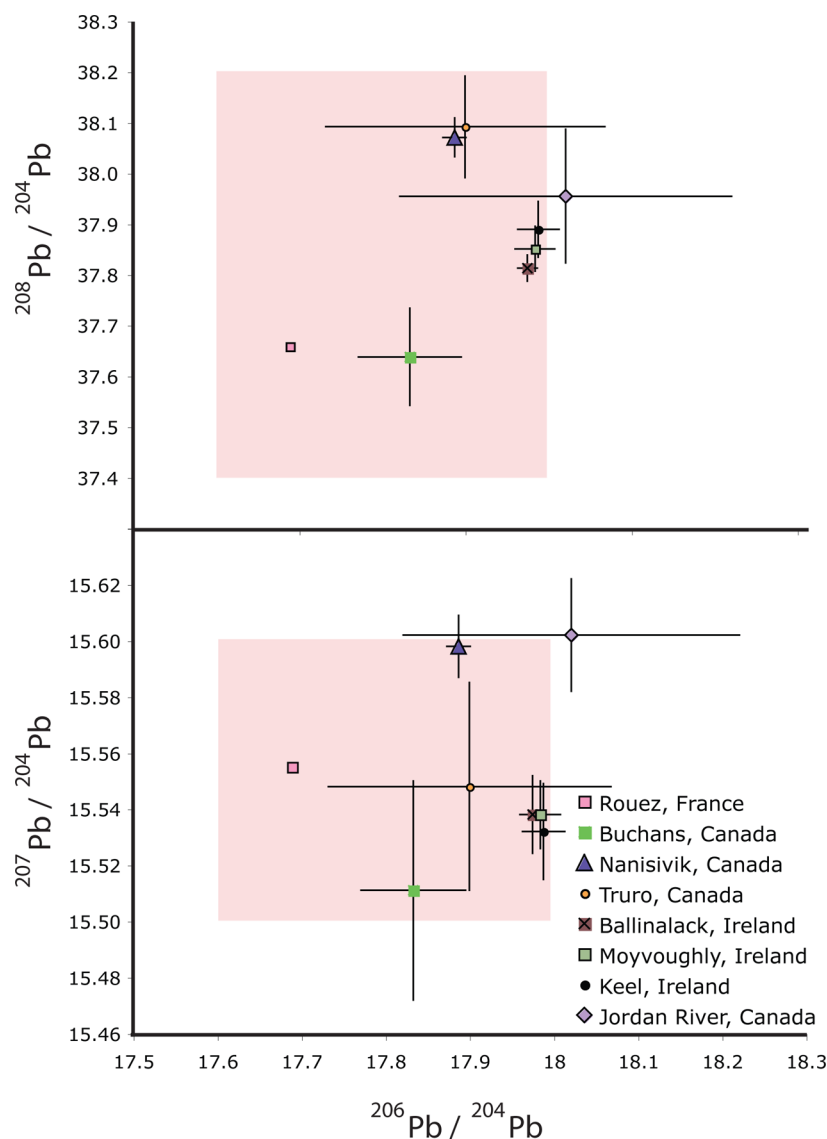


Figure 6. Pb–Pb isotope plots that compare the estimated “Trinity” Pb isotopic signature (red box) to those for major Pb ore deposits (mines) worldwide¹⁵ that are characterized by similar/overlapping Pb isotopic compositions.

the Holmes–Houtermans^{23,24} model assumes a single-stage Pb evolution in the Earth’s mantle, while the Allègre et al.²² and Stacey–Kramers²⁵ models assume multiple stages of Pb growth. Based on the estimated Pb isotope composition of the Trinity-related anthropogenic component (Figures 4 and 5), the various models yield a large range of model ages that vary between a “future” age,^{23,24} 400 Ma,²² and 525 Ma.²⁵ Despite the relatively large range of model ages, the calculations do provide a maximum age for the industrial ore deposit that sourced Pb used within the Trinity-related components. In this case, the oldest possible age of the ore deposit is 525 Ma, and this estimate provides a first “filter” for determining the source of the anthropogenic Pb used within the Trinity test.

Sourcing the Pb Ore. Sangster et al.¹⁵ compiled a database of all large-scale industrial Pb sources worldwide for the purpose of tracing Pb (pollution) in the environment and other large-scale anthropogenic uses of Pb. Comparison of the estimated Trinity Pb isotope composition (Figures 4 and 5) to possible, significant sources of industrial Pb worldwide¹⁵ yields several possible matches including Rouez in France; Buchans, Nanisivik, Truro, and Jordan River in Canada; and Ballinalack,

Moyvoughly, and Keel in Ireland (Figure 6). However, upon detailed investigation, only one mine was active at the time before and during the Trinity test and, therefore, is the only reasonable candidate. The Pb isotopic composition of the Buchans mine²⁷ is in agreement with the estimate for the anthropogenic Pb contained within the Trinity test-related components (Table S2 in Supporting Information, Figure 6). Interestingly, the deposit is located in Newfoundland, Canada, but was mined by American Smelting and Refining Company (ASARCO) from 1928 to 1984, within the time frame associated with Trinity test-related activities. During the period of time ASARCO owned the Buchans mine, ~16 million tons of 7.56% head grade Pb was mined.²⁸ Hence, it is possible that the source of the industrial Pb used in the Trinity test was derived from the Buchans mine. It should be stated that an undocumented Pb mine with similar isotopic composition could have been the source for the Pb in the Trinity test; however, there is no evidence in the literature supporting the exploitation of a lead mine during the 1940s–1950s containing the same lead isotopic composition as determined in our work and as reported for the Buchans mine.²⁷

CONCLUSIONS

The Pb isotopic compositions of trinitite melt glass reveal that the anthropogenic Pb used in the Trinity test is derived from an industrial Pb ore deposit. There is no supporting documentation available in the literature for this result; however, Pb bricks, solder, pigs, or another anthropogenic component could have easily been used during the test and may not have been explicitly acknowledged. The Pb isotopic signature of postdetonation nuclear materials from the Trinity site is estimated on the basis of the positive correlation between Pb and Cu abundances; the latter has been interpreted as derived from anthropogenic sources. The Pb isotopic composition of the industrial Pb used in the Trinity test is from a geological deposit with a maximum age of 525 Ma. Finally, the isotopic composition of the device-related Pb employed within the Trinity test coincides with that from the Buchans mine in Newfoundland, Canada. This mine was active during the time of the Manhattan project (1940s–1950s) and operated by an American company, which could have easily provided industrial Pb for components/materials used in the Trinity nuclear test.

ASSOCIATED CONTENT

Supporting Information

Two tables, listing instrument settings and cup configurations and Pb isotopic compositions of trinitite glass, pristine feldspar, estimated device, and Buchans mine. 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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