Evaporative fractionation of zinc during the first nuclear detonation

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Volatile element and compound abundances vary widely in planets and were set during the earliest stages of solar system evolution. Experiments or natural analogs approximating these early conditions are limited. Using silicate glass formed from arkosic sands during the first nuclear detonation at the Trinity test site, New Mexico, we show that the isotopes of zinc were fractionated during evaporation. The green silicate glasses, termed “trinitite,” show +0.5 ± 0.1‰/atomic mass unit (amu) isotopic fractionation from ~200 m to within 10 m of ground zero of the detonation, corresponding to an α fractionation factor between 0.999 and 0.9995. These results confirm that Zn isotopic fractionation occurs through evaporation processes at high temperatures. Evidence for similar fractionations in lunar samples consequently implies a volatile-depleted bulk Moon, with evaporation occurring during a giant impact or in a magma ocean.

INTRODUCTION

The inventory of volatile elements and compounds in planetary bodies plays a crucial role in their evolution, fundamentally altering melting and differentiation processes (1, 2), generation and sustainability of atmospheres and oceans (3), and planetary habitability. Element volatility is typically defined by the 50% condensation temperature (TC50), calculated at a total pressure near 1 astronomical unit (1.5 × 10^8 km) in the solar nebula of 10^-3 bar (4). Volatiles include both low-boiling point compounds (for example, H2O, CO2, CH4, SO2, and NH3), as well as elements with atmophile (TC50 < 200 K; H, C, N, O, and noble gases), highly volatile (TC50 < 646 K; for example, Cl, S, Se, Sn, and Pb), and volatile to moderately volatile characteristics (TC50, 665 to 1134 K; for example, K, Zn, Rb, P, and Cs). Understanding planetary processes requires knowledge of the behavior of volatile elements and compounds and how and when they were added or lost from planetary bodies.

Constraints have been placed on planetary volatile inventories using atmophile elements and water, but these elements and compounds tend to have highly incompatible characteristics during melting of planetary interiors (5), becoming ice, liquid, or vapor at planetary surfaces, greatly complicating estimations of planetary volatile inventories. Conversely, many volatile and moderately volatile elements are also lithophile elements, remaining in rock-forming minerals and melts. In particular, the moderately volatile element zinc (TC50, 726 K) is a tracer of planetary volatile histories, because it behaves predictably during planetary melting (6), and has five stable isotopes ([64Zn, 66Zn, 67Zn, 68Zn, 70Zn]), making it possible to investigate kinetic or equilibrium isotopic fractionation effects (7) during evaporative fractionation. It has been demonstrated that there is a strong depletion of Zn in the Moon, compared with Earth, implying significant volatile loss during lunar formation (8–10). However, it has also been shown that Zn isotopic fractions (expressed as δ56Zn = ([56Zn/64Zn]sample/[56Zn/64Zn]JMC Lyon – 1) × 1000, where 56Zn equals either 64Zn, 68Zn, 70Zn, or 70Zn) of planetary materials do not perfectly match predicted fractionations of the isotopes during kinetic processes but, rather, follow subdued fractionations that approach unity (6).

Experimental evidence of this effect has yet to be demonstrated for zinc but has been found in potassium, from ~10^-9 to 1 bar (11, 12), with the results possibly consistent with fractionation factors close to unity at high pressures (13).

A major impediment in interpreting volatile element isotope fractionations has been the fact that laboratory experiments are either unable to reproduce the scale or temperatures consistent with planetary-scale volatile processes, or are lacking for many elements, making empirical assessment of isotopic fractionation and volatile element loss challenging. This is a particular problem because studies of volatile compounds, such as water or OH in lunar glasses, suggest that the Moon may have volatile element abundances approaching Earth’s upper mantle composition (14, 15); other studies have suggested localized volatile loss from the Moon (16), in contrast to the large-scale processes of volatile loss suggested for Zn (6, 8, 9) and K (13).

To empirically constrain the isotopic fractionation factor of Zn and the behavior of moderately volatile elements during evaporative fractionation, we have investigated Zn isotope and trace element abundances in trinitite glasses from the Trinity test site, New Mexico, USA. The Trinity test site was the location of the first nuclear detonation, on 16 July 1945. The 239Pu implosion device (Y-1561), known as the “Gadget,” exploded with the equivalent force of 84 TJ, creating local conditions at the site of 8430 K and >8 GPa, and localized vaporization of the arkosic desert sand. Vaporization, melting, and redistribution of the sand led to the formation of a thin sheet of dominantly green-colored glass that extended approximately 300 to 350 m from ground zero, beneath the Gadget (17). The Trinity test site is a large-scale “experiment” for understanding volatile processes occurring at temperatures and/or pressures relevant to those found during planetary formation.

RESULTS

Samples investigated in this study include trinitite taken within 10 m of ground zero (IF), at 100 m (IG), and within 150 to 250 m (trinitite I (T1), T2, and T3). For samples IF and IG, Xe isotope abundances were measured, allowing estimation of the cooling rate and temperatures of formation of the glass. The 10 m sample, IF, formed at 1663 K and cooled within 17 min of emplacement, while the 100 m sample, IG, formed at 1593 K and cooled within 5 min of emplacement (18). Peripheral samples (T1, T2, and T3) likely formed at lower temperatures and higher rates of cooling, and samples T2 and T3 had
quantities of unmelted desert sand adhering to them. Although maximum conditions at the nuclear test site were exceptionally high (8430 K), we consider the bound of 1663 K as the maximum temperature condition for the formation of the trinitite glasses. By using the Clausius-Clapeyron relationship, this equates to ≤0.2 GPa of vapor pressure in the desert air.

Trinitite samples have similar abundances of refractory elements (TC50 >1600 K), regardless of distance from ground zero, save for variations of U and Th abundances (Fig. 1). Trinitite occurs in a variety of colors and differing morphologies, with evidence that red trinitite formed with enhanced abundances of Fe, Cu, and Pb inherited from copper cables, lead bricks, and the iron steel tower holding the bomb casing materials in place at the test site (19). Likewise, U, Th, and Pb excesses in some green trinitite glasses have been related to the presence of bomb materials (20). Significant differences in Fe, Zn, Se, and Ge abundances occur between the “proximal” 10 m (IF) and 100 m (IG) trinitite glasses, compared with the peripheral trinitite glasses (T1, T2, and T3). Remarkably, Fe is lower in the IF and IG trinitite glasses despite their close proximity to the steel tower that held the Gadget in place, in contrast to the metal-rich red trinitite (19).

Zinc isotope fractionation with distance from the Gadget
A remarkable feature of the Zn isotope compositions of trinitite is that it correlates (R2 = 0.8) with the distance from ground zero at the Trinity test site (Fig. 3). With increasing distance from ground zero, Zn abundances increase and δ66Zn decreases. The least-melted and peripheral trinitite sample (T3) has δ66Zn values similar to those of the arkosic desert sand at ~0.2 to 0.25‰, which is within uncertainty of estimates of terrestrial igneous rocks (21). Extrapolation of the trend in δ66Zn versus distance from the Gadget indicates that the average arkosic sand composition is ~0.2‰, consistent with the least-melted trinitite sample. Conversely, δ66Zn values for sample IF, 10 m from ground zero, are between 0.4‰ (bulk versus bulk) and 0.6‰ (residue versus residue) heavier than the least-melted trinitite. Collectively, these results indicate evaporative loss of zinc, as well as of some other volatile elements depleted in the proximal trinitites (Se, Ge, and possibly Fe), with distance from the epicenter of the nuclear detonation. Given these conditions, isotopically light δ66Zn values for leachates can be interpreted as condensate vapor that collected on the trinitite glass during cooling in the aftermath of the nuclear detonation.

Natural analogs and empirical fractionation factors
Some natural analogs approach conditions required for volatile loss in planets. For this reason, we consider their suitability for calculating empirical fractionation factors. Glasses formed through lightning strikes, called fulgurites, can be formed at reducing conditions at pressures up to 25 GPa and temperatures of 2000 K (22); however, fulgurites are also formed locally (103 to 105 m) and in the ground, potentially leading to chemical buffering effects with the surrounding soil. No data are currently available for these samples for Zn isotopes. Larger-scale natural analogs include tektite glasses. Tektites form through meteoroid collisions with the Earth’s atmosphere, leading to extreme heating (>2273 K), pressure (4 to 100 GPa), reduction, and potentially localized atmospheric blow-off (23), generating glasses with compositions similar to those of soils (24). Tektites show progressive enrichment in Zn isotope composition with decreasing Zn abundance, consistent with fractionation due to evaporation and progressive volatile element loss during their formation (25). As with studies of lunar

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**Fig. 1.** Incompatible trace element abundances in trinitite glasses, ordered according to TC50, double-normalized over the least-melted trinitite sample (T3) and strontium. TC50 are from a study by Lodders (4), with shaded boundaries shown for elements with TC50 of >1600, >800, and <800 K.

**Fig. 2.** δ66Zn versus δ68Zn for trinitite samples and for their associated residues and leachates or etchates. Solid line illustrates the predicted mass-dependent fractionation curve of 2. Shaded bars define the terrestrial Zn isotope composition from a study by Chen et al. (21). R, residues; L, leachates or etchates.
Possible evidence for isotopically light Zn on the surface of trinitites at the Trinity test site suggests that the latter mechanism would predict empirically derived fractionation factors (1, 0.9998, 0.999, and 0.998) for arkosic sand at the Trinity test site. The evidence for evaporative fractionation of Zn and other volatile and moderately volatile elements, combined with the presence of high water contents in some lunar basalts, implicates heterogeneous distribution of volatiles in the lunar mantle inferred from Zn/Fe variations (10).

Evaporation of volatile elements from the Moon

The new results from trinitite provide the first definitive evidence for evaporative fractionation of Zn during high-temperature conditions and are consistent with subdued fractionation factors for Zn. Pressure conditions are more difficult to ascertain, but elevated pressures are likely during planetary formation (13) or during global magma ocean phases on planetary bodies, when volatile loss led to nascent atmospheres (6). These results strongly support the loss of Zn and other volatile and moderately volatile elements through evaporative fractionation effects during the formation and evolution of the Moon, as well as other planetary bodies.

Studies of Zn, Cl, S, and K isotopes in lunar materials (6, 8, 9, 13, 16), OH contents in apatites from lunar mare basalts (26), and moderately volatile element abundance in mare basalts (10, 27) imply a volatile-depleted Moon. These results contrast with evidence from the Apollo high-Ti lunar glass 74220 that implies a lunar interior with water contents similar to those of Earth’s mantle (14, 15). Mechanisms for evaporative loss of volatile elements consistent with available Zn isotope data include a giant impact (8) or loss from a magma ocean (6). Possible evidence for isotopically light Zn on the surface of trinitites at the Trinity test site suggests that the latter mechanism would predict the presence of isotopically light condensates on the lunar surface, and more heterogeneous distribution of volatiles within the Moon. In contrast, giant impact evaporative loss would imply homogeneous “dry out” of materials accreting to form the Moon. The evidence for evaporative fractionation of Zn and other volatile and moderately volatile elements, combined with the presence of high water contents in some lunar samples, implicates heterogeneous distribution of volatiles in an otherwise “dry” Moon.

MATERIALS AND METHODS

Samples

T1, T2, and T3 are samples from the periphery of the affected blast site, with an estimate distance of 200 ± 50 m. T3 had the least amount of trinitite glass, and we used this sample to estimate background trace
Zinc isotopic and abundance measurements

We used methods for the purification and isotopic measurement of Zn, as described previously (28). Samples were dissolved in a 4:1 mixture of ultrapure HF/HNO3 in Teflon beakers for 4 days. Zinc purification was achieved using anion exchange chromatography, with a recovery of 99 ± 1%. The samples were loaded in 1.5 N HBr on 0.25-ml AG-1X8 (200 to 400 mesh) ion exchange columns, and Zn was collected in 0.5 N HNO3. The Zn fraction was further purified by eluting the samples twice on a 100-μl column, with the same eluting solutions. The blank measured with samples was 5 ng, in line with our previous work (8, 9), and generally represents less than 2% of total measured Zn for most samples, except for some of the low-Zn abundance leaches (table S1).

Zinc isotopic compositions were measured on the ThermoElectron Neptune Plus Multicollector Inductively Coupled Plasma Mass Spectrometer, housed at the Institut de Physique du Globe de Paris. The Faraday cups were positioned to collect the masses 62, 63, 64, 65, 66, 67, and 68. Possible 64Ni isobaric interferences were monitored and corrected by measuring the intensity of the 64Ni peak. A solution containing 500 parts per billion (ppb) of Zn in 0.1 M HNO3 was prepared for isotopic analysis and was matched with 500-ppb standard solutions. Isotopic ratios of Zn in all samples were analyzed using a spray chamber combined with a PFA nebulizer at 100 μl/min. One block of 30 ratios was collected for each individual sample measurement, in which the integration time of a single scan was 10 s. The background was corrected by subtracting the on-peak zero intensities from a blank solution. Instrumental mass bias was corrected by bracketing each of the samples with standards. External precision based on the JMC Lyon Zn standard was 0.04 %/amu (atomic mass unit) (2σ) for δ66Zn and 0.09 %/amu (2σ) for δ67Zn and δ68Zn. Values of δ66Zn, δ67Zn, and δ68Zn were found to be within uncertainty for the JMC Lyon Zn standard and IRMM Zn metal (table S1).

Trace element abundances

Whole-rock powders were measured for bulk-rock trace element abundances at the Scripps Isotope Geochemistry Laboratory. Samples were digested at 150°C in Optima-grade concentrated HF (4 ml) and HNO3 (1 ml) for >72 hours on a hot plate, with total analytical blanks and terrestrial basalt standards. Samples were sequentially dried and taken up in concentrated HNO3 to remove fluorides, followed by dilution and doping with indium to monitor instrumental drift during analysis. Trace element abundance analyses were done using a Thermo Scientific iCAP Qc quadrupole inductively coupled plasma mass spectrometer in standard mode. Analyses were standardized versus reference material BHVO-2 that was measured throughout the analytical run. In addition, reference materials were analyzed as “unknowns” (BHVO-2 and BCR-2) to assess matrix matching, external reproducibility, and accuracy. For trace elements, reproducibility of the reference materials was generally better than 5% (relative SD) and in line with standard data measured in the laboratory (29).

References and notes

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