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Diffusive Mass Transport in Agglomerated Glassy Fallout from a Near-Surface Nuclear Test

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0. Abstract

Aerodynamic glassy fallout is formed when vapor phase constituents from the nuclear device are incorporated into molten carriers derived from soil or other near-field environmental debris. The effects of speciation and diffusive transport of condensing constituents are not well defined in models of fallout formation. Previously we reported observations of diffuse micrometer scale layers enriched in Na, Fe, Ca, and $^{235}$U, and depleted in Al and Ti, at the interfaces of agglomerated fallout objects. Here, we derive the timescales of uranium mass transport in such fallout as it cools from 2500 K to 1500 K by applying a 1-dimensional planar diffusion model to the observed $^{235}$U/$^{30}$Si variation at the interfaces. By modeling the thermal transport between the fireball and the carrier materials, the time of mass transport is calculated to be <0.6 seconds, <1 second, <2 seconds, and <3.5 seconds for fireball yields of 0.1 kt, 1 kt, 10 kt, and 100 kt respectively. Based on the calculated times of mass transport, a maximum temperature of deposition of uranium onto the carrier material of ~2200 K is inferred (1σ uncertainty of ~200 K). We also determine that the occurrence of micrometer scale layers of material enriched in relatively volatile Na-species as well as more refractory Ca-species provides evidence for an oxygen-rich fireball based on the vapor pressure of the two species under oxidizing conditions. These results represent the first application of diffusion-based modeling to derive material transport, thermal environments, and oxidation-speciation in near-surface nuclear detonation environments.

1. Introduction
In near-surface nuclear explosions, aerodynamic glassy fallout is produced by the mixing of vaporized device and environmental materials into molten carriers derived from soil and other nearby materials, which quench before coming in contact with the ground (Glasstone and Dolan, 1977). Vaporized materials can either condense directly onto the surface of molten carriers, or can be deposited as already condensed droplets onto the surface of carriers. The condensed material is subsequently mixed into the molten material by diffusion and mechanical mixing (Miller, 1960; Freiling, 1965; Freiling, 1970). The effect of the speciation on condensation and diffusion in fallout materials is poorly understood, but remains fundamental to dispersion models predicting the composition and dispersion of radioactive fallout.

Historic fallout formation theories combine physical models with empirical relationships derived from early atmospheric tests (Freiling, 1959; Miller, 1960; Norment, 1979). Refractory species are thought to volumetrically incorporate into carrier materials by mechanical mixing, while volatile species deposit onto the surface of the solidifying carriers. These models consider physical principles such as gas-phase diffusion of species in the fireball, condensation onto and diffusion within carriers, as well as re-evaporation of condensing species under the assumption of equilibrium conditions. Such models do not, however, consider heat transfer from the fireball to the carriers, nor the effect of speciation on condensation and diffusion, both of which affect the rates of condensation onto, and diffusion through, the molten carriers. The potential importance of speciation on the condensation and mixing process is underscored by recent work analyzing the uranium isotopic composition of fallout, which found both inter- and intra-sample heterogeneity (Eppich et al., 2014; Lewis et al., 2015; Weisz et
In the context of fallout formation models, uranium, if present in an oxide form, may condense first and mix volumetrically into molten carriers due to the refractory nature of uranium oxides (Miller, 1960, Freiling 1965). Stable xenon isotope ratios measured in aerodynamic fallout glass provide evidence that reducing conditions attend at least some phases of fallout formation (Cassata et al., 2014), although recent findings suggest that multiple different oxidation states of U and Fe may be preserved in fallout (Giuli et al., 2010, Pacold et al., 2016). The chemical and isotopic heterogeneity of uranium observed in fallout samples suggests that vapor-phase speciation due to varying redox conditions may be primarily controlled by the amount of air entrained into the fireball, and possibly buffered, to a first order, by the magnitude and speciation of iron present in the vapor phase (Pacold et al., 2016). Clearly, the oxidation state of vapor-phase constituents will impact the condensation and evaporation behaviors in an evolving fireball environment as fallout forms.

The interfaces between fused glassy fallout objects can preserve late stage condensation features, including diffusion profiles, (Weisz et al., 2017). In the population of samples studied, these interfaces are characteristically enriched in sodium, iron, calcium, and uranium, and depleted in aluminum and titanium. Similar enrichments of Fe and Ca have been observed in suspected anthropogenic contributions to trinitite glass (Bellucci et al., 2016). The co-location of volatile and refractory elements at the interface implies that after initial condensation, fallout formation continues through a fractionation and diffusion process dictated by the speciation of vapor-phase constituents, and may be affected by contributions from anthropogenic materials (Weisz et al., 2017).
Understanding speciation in the vapor phase is essential to establishing a comprehensive model of fallout formation. In this study, we show that the diffuse interfaces observed between agglomerated fallout objects preserve a record of the thermal histories experienced prior to quenching in the fireball. To demonstrate and explore this record, we apply a model of one-dimensional planar diffusion to explain the Gaussian distribution of uranium concentration observed at select agglomerate interfaces. Subsequently, we estimate the time and temperature over which uranium diffusion occurred from this interface. By constraining the time and temperature of mass transport, the deposition temperature of late stage vapor species onto fallout surfaces prior to agglomeration is also constrained. We then use these insights to interpret the source and speciation of vaporized constituents, and the redox conditions of the fireball.

2. Modeling methodology and results

2.1 Data selection

The dataset used for diffusion modeling is derived from agglomerated fallout glasses originating from a uranium-fueled near-surface nuclear test (Weisz et al. 2017), and acquired by nano-scale secondary ion mass spectrometry (NanoSIMS). The sample set consists of mm-scale aerodynamic glassy objects with approximately rhyolitic major element compositions. The objects include numerous sub-mm secondary objects fused to the surface of larger glassy objects (Figure 1). Deposition layers at the interfaces of the fused objects were identified using backscatter electron imaging. NanoSIMS ion images were collected at these interfaces showing micro-scale compositional relationships and $^{235}\text{U}/^{30}\text{Si}$ variation (Figure 1).
Of the nine interfaces presented in Weisz et al. (2017), three of these yielded approximately Gaussian distributions of $^{235}\text{U}/^{30}\text{Si}$ profiles. In the case of a thin layer of condensed species deposited onto the surface of a molten carrier that subsequently fuses with a larger molten object, the deposited layer is expected to diffuse into both objects if there is a chemical potential gradient between the layer and the molten objects. In the idealized case, that the layer comprises a single species, is infinitesimally thin, and is between two homogeneous objects of equal composition. The concentration distribution will evolve from the layer between two objects of equal temperature over time, following the Gaussian form of

$$C(x, t) = C_0 e^{-\frac{x^2}{4Dt}}$$  \hspace{1cm} (1)

where $C$ is concentration, $C_0$ is the initial concentration of the species in the layer, $D$ is the diffusivity, $t$ is time, and $x$ is the dimension of diffusion (Zhang, 2010). Based on these observations, three approximately Gaussian $^{235}\text{U}/^{30}\text{Si}$ profiles B1, C1, and D2 were chosen as the focus of the diffusive modeling presented, here.

The experimentally determined $^{235}\text{U}/^{30}\text{Si}$ ratio profiles at the three chosen interfaces were fit in IGOR Pro software using non-linear least squares regression analysis with a modified Gaussian function:

$$G = A + Bx + Cx^2 + \frac{E}{\sigma\sqrt{2\pi}} e^{-\frac{(x-\mu)^2}{2\sigma^2}}$$  \hspace{1cm} (2)

where $\sigma$ is the standard deviation of the distribution, $\mu$ is the mean of the distribution, $E$ is a fit scaling parameter, and $A+Bx+Cx^2$ is a quadratic expression (with fitting coefficients $A$, $B$, and $C$) added to allow for minor compositional variation on either side of the interface and still acquire a Gaussian fit of the peak. The compositional data at these interfaces were confirmed to approximate Gaussian distributions, and are shown
with their modeled fits in Figure 2. Full details on the original samples and analyses, as well as the sample naming scheme, are contained in (Weisz et al., 2017), and the use of the data with our model approach is described, below.

### 2.2 Mass and thermal transport

In Figure 3, the interface region is shown to be narrow (<10 micrometers) in comparison to the (mm-scale) host fallout object, indicating that 1-D planar diffusion is an appropriate approximation. Mass transport of uranium at fused fallout interfaces can therefore be approximated using one-dimensional planar diffusion. In the one-dimensional planar diffusion model, the concentration distribution follows the relation

\[
C(x, t) = C_0 e^{-\frac{x^2}{4Dt}},
\]

where \(C\) is concentration, \(C_0\) is the initial concentration of the species in the layer, \(D\) is the diffusivity, \(t\) is time, and \(x\) is the dimension of diffusion (Zhang, 2010).

Applying the Gaussian form of Equation (3), the standard deviation (\(\sigma\)) from fits of the \(^{235}\text{U}/^{30}\text{Si}\) profiles acquired using Equation (2) yields a convolved parameter of average diffusivity and time (\(D_{avg} t\)) over a given period of mass transport,

\[
\sigma = \sqrt{2D_{avg} t},
\]

where \(D_{avg}\) is the average diffusivity over a temperature interval in the medium, presented in Table 1. As diffusivity is temperature dependent according to the Arrhenius equation, we can derive an expression of

\[
\frac{\sigma^2}{2} = D_{avg} t = \int_{t_1}^{t_2} D_0 e^{\frac{-E_a}{RT(t)}} dt,
\]

where \(t_1\) is the temperature of initial deposition of material at the interface, \(t_2\) is the temperature at which mass transport effectively stops, \(T(t)\) is the cooling rate of the
medium, and $D_o$ and $E_a$ are the respective pre-exponential constant and activation energy of the diffusant.

The most pertinent parameters of $D_o$ and $E_a$ for uranium diffusion in rhyolitic material in the literature are $363.8\pm24.0$ kJ/mol and $e^{2.51\pm0.35}$ cm$^2$/s, respectively (Mungall and Dingwell, 1997). In that study $D_o$ and $E_a$ values were derived as effective binary uranium diffusion parameters determined in a haplogranitic melt (79% SiO$_2$, 12% Al$_2$O$_3$), and assuming uranium to be in the hexavalent state. For our model we also assume uranium in the hexavalent state, as supported by recent work using X-ray absorption near edge structures (XANES) on melt glass from a uranium-fueled test (i.e., UO$_2^{2+}$; Pacold et al., 2016).

In order to acquire a deposition layer of condensed material at the interface of two fused objects, at least their surfaces were in the liquid state when the layer was deposited and before the objects collided, subsequently solidifying before significant ground interaction. It follows that the cooling rate of the interfaces (where the still molten objects collided) would be controlled by the cooling rate of the fireball. Thus, the cooling rate of the medium (i.e., the molten host object) is considered by computationally modeling thermal transport in a rhyolitic material approximating the shape of two fused spherical fallout objects under cooling fireball conditions using the finite element analysis software, COMSOL (Figure 4). This model simulates two spherical objects that fused together, with the larger object having a diameter of 1.5 mm, and the smaller object having a diameter of 0.4 mm. As shown in the 3-dimensional model, the smaller object is partially embedded in the larger object. In this model, the 'interface' was defined as the outer edge of the larger sphere within the smaller sphere.
The cooling rate of the fireball was modeled using Hillendahl’s equations based on light output curves (Freiling et al., 1965) to provide the yield-dependent fireball cooling rate:

$$-\frac{dT}{dt} = 776W^{0.10}t^{-1.34} \approx (3 \times 10^{-11})W^{-0.3}T^4 \quad (4)$$

where $T$ is temperature in K, $W$ is the yield in kt, and $t$ is time (in seconds). The fireball cooling rate is then modeled for a range of fireball yields of 0.1 kt, 1 kt, 10 kt, and 100 kt, to generalize results to a range of potential near-surface events.

Expanding upon Freiling’s 1965 approach, the heat transfer model applied to this system includes conductive, convective, and radiative heat transfer between the fireball and the molten material. Conduction was used to model heat transfer within the molten material, while convective and radiative heat transfer were used to model the external effect of the cooling fireball environment on change in temperature within the modeled fallout object (Fig. 5). The cooling curves at the interface point of the fused objects (Figure 5) were determined for yields of 0.1 kt, 1 kt, 10 kt, and 100 kt from boiling point of SiO$_2$ (2500 K) to the solidification temperature (1500 K) of fallout glass (Freiling et al., 1965). The cooling curves serve as the input for $T(t)$ in Equation (3). Resultant values for the time that diffusion from the interface effectively stops ($t_2$) for 0.1, 1, 10, and 100 kt yields were calculated to be approximately 3, 4, 8, 10 seconds, respectively. Setting a pre-defined end time ($t_2$) as the time at which the interface reaches 1500 K (and mass transport effectively stops), we then solved for $t_1$, or the time of deposition along the cooling curve for a given yield in the series.

2.3 Probability distributions for the time of deposition
Using Equation (3), the $D_{avg}$ parameters (Table 1), in combination with the cooling equations $T(t)$ for the interfaces at each modeled fireball yield (Fig. 4), enables determination of the time of deposition $t_1$ for each of interfaces B1, C1, and D2. However, Equation (3) cannot be analytically solved for deposition time $t_1$ and there are uncertainties on the values of $D_0$, $E_a$, and $D_{avg}$. Instead, cumulative probability distributions for $t_1$ were numerically generated, taking into account these uncertainties, and subsequently used to determine the model time of deposition $t_1$ and its uncertainty.

To generate the cumulative probability distributions for the value of deposition time $t_1$, the probability of model success was determined for 100 pre-defined values of $t_1$ (equal time-steps between $t_1=0$ and $t_1= t_2$, exemplified in Figure 6). The model was deemed successful if the calculated cooling interval ($t_2-t_1$) was sufficiently long to produce the observed diffusion profile, thus satisfying the relation

$$\int_{t_1}^{t_2} D_0 U e^{-\frac{E_a U}{RT(t)}} dt \geq D_{avg} t$$

(6)

At each time-step, the probability of model success was determined by generating 1000 randomly selected values from normal distributions of the values of $D_0$, $E_a$, and $D_{avg}$, based on their means and uncertainties. Each cumulative distribution function was fit with an error function, from which the average value ($\mu_{t_1}$) and standard deviation ($\sigma_{t_1}$) of $t_1$ was determined for the yield-series at each interface. A total of 12 cumulative distribution functions for the value of $t_1$ were calculated (3 interfaces at 4 different yields; Table 2).

### 2.4 Temperature of deposition

Using the calculated values of $\mu_{t_1}$ and $\sigma_{t_1}$, the temperature of deposition $T_{dep}$ was determined for each interface using the respective cooling curves for each yield (see...
The values for $t_1$ have normally distributed uncertainties ($\sigma = \text{standard deviation}$); however, because the cooling curves are exponential functions, the uncertainties on $T_{dep}$ simply represent the temperature interval that corresponds to $1\sigma$ uncertainty on $t_1$.

The time and temperature of deposition between the interfaces at each corresponding yield show essentially no variation (the values are within $1\sigma$ uncertainty). There is, however, substantial relative time variation between each yield in the series, ranging from about 0.5 seconds at 0.1 kt to about 3.4 seconds at 100 kt. This corresponds to a difference in the calculated average temperature of deposition of approximately 150 K between the highest and lowest measured yield for each studied interface.

3 Discussion

3.1 The effect of heat transfer between the fireball and the carrier materials

Our computational modeling reveals that thermal transport of species in the fireball into molten carrier materials can have a significant effect on the cooling rate used in diffusion modeling (Figure 7). For example, in a 1 kt fireball cooling from 2500 K, a carrier material initially at thermal equilibrium with the fireball will take roughly twice as long to cool 1500 K in comparison to the average fireball temperature. This difference in
cooling rate not only affects estimates of mass transport, but also the calculated temperature of late stage deposition of bomb vapor species onto molten fallout objects.

While historical fallout formation theories such as by Miller (1960) and Freiling (1965) model interdependent, physicochemical phenomena such as condensation, fractionation, and incorporation of radionuclides, they do not consider heat transfer between the fireball and the carrier materials. Freiling et al. (1965) specifically describe effects of mass transport in a cooling fireball environment, including diffusion and re-evaporation from the surface. Both are temperature-dependent processes that control the composition of resultant fallout. Thus, any first-principles fallout formation model must take into account the effect of thermal transport on temperature-dependent mass transport into molten carrier materials.

Mass transport and the efficacy of this mechanism for introducing bomb vapor into carrier materials is also dependent on the condensation temperature and the diffusivity of individual species in the vapor. As diffusion is controlled both by thermal and chemical gradients, the Gaussian profiles selected for 1-D diffusion modeling indicate that, at the time of collision of the small droplet and large droplet, the temperature and compositional difference between these two objects was negligible, at least near their respective surfaces. Considering a scenario where both objects were approximately the same composition and temperature, species enriched at the interface would diffuse at the same rate into either object, forming a symmetrical profile. We conclude that these samples, characterized by symmetrical interfaces and similar $D_{avg}$ values (Table 2), were likely at similar temperatures prior to collision, and did not experience significant re-evaporation from the surface.
From this limited sample set that similarly sized fallout objects may have experienced different time-temperature histories prior to quenching. The consistency in the widths of the $^{235}\text{U}/^{30}\text{Si}$ distributions at the interfaces targeted in this study, however, suggests the thermal conditions of deposition of material at the interface and subsequent mass transport into the carriers were similar. By selecting interfaces with Gaussian concentration distributions, indicating that host and agglomerated object boundaries were at similar temperature at the time of collision, we limit the sensitivity of our diffusive modeling to temperature heterogeneities in the fireball.

3.2 Constraining the timescale of mass transport and temperature of deposition

Through diffusion modeling, we estimate the time of mass transport from the observed deposition layers ($\Delta t$) of 2 seconds, 3 seconds, 4.5, and 7 seconds for the 0.1 kt, 1 kt, 10 kt, and 100 kt yield models, respectively. These values are comparable to glassy fallout cooling estimates by Bonamici et al., (2017) in objects of similar dimension from the Trinity test. In that study, however, cooling timescales were acquired from diffusive modeling of Si between different compositional phases within trinitite samples, without taking into consideration heat transfer between the fireball and the molten objects. Given that our study focuses on mass transport at sample surfaces, surface-closure times of <3 seconds calculated by Cassata et al. (2014) may be more directly relevant. These overlapping timeframes of mass transport strongly suggest that incorporation of fission products, unfissioned device materials, and other vaporized constituents into aerodynamic glassy fallout objects occurs over the course of a few seconds. Cassata et al. (2014) posit two possible scenarios explaining this rapid closure time: either the location
in the fireball where the fallout formed cooled to 1500 K within ~3 seconds, or the
molten fallout precursors were ejected from the fireball and rapidly quenched within ~3
seconds. The cooling times modeled for each yield series is consistent with average
fireball temperatures reaching quenching temperatures within seconds, but does not
preclude quenching upon ejection.

Modeling a range of yields not only enables generalization of mass transport
timescales in a variety of potential nuclear event scenarios, but also bounds the maximum
temperatures of deposition. The temperatures of deposition for each hypothetical yield
(Fig. 9) were fit by linear least squares regression for each interface, and show a
maximum average temperature of deposition of $2185 \pm 167$ K.

The temperature of deposition derived from modeling of the data increases inversely
with hypothetical yield (Table 2 and Fig. 9). This observation is not unexpected, as the
fireball cooling rates are yield-dependent (See Electronic Annex 1, section EA1.3)
Correspondingly, in order to acquire the same diffusion profile as a function of increasing
yield, the temperature at the time of deposition would have to be higher. Within the
resolution of current measurements, however, this effect is minimal. These data show that
the determined temperature of deposition does not vary significantly as a function of
fireball yield. Specifically, for each of the modeled interfaces, the average temperature of
deposition changes by only ~150 K between the 0.1 kt and 100 kt models (Table 2),
representing 4 orders of magnitude variation of modeled yield (Fig. 9).

3.2 Speciation of vaporized constituents

Fallout formation models assert that refractory species will condense and incorporate
into molten carrier materials via mechanical mixing or diffusion, whereas volatile species
deposit at lower temperatures onto the surface of already quenched carrier materials (Miller, 1960). The interfaces of agglomerated fallout objects preserve characteristic co-located enrichments of some refractory species (*i.e.*, calcium, iron, uranium) and depletion in others (*i.e.*, aluminum and titanium), indicating a co-deposition of Ca, Fe, and U species (Weisz *et al.*, 2017, Table 3). The refractory oxide species, FeO and CaO, are likely derived in part from the local soil as well as from additional anthropogenic sources (Weisz *et al.*, 2017). Both vaporize at around 3000K (Cornell and Schwertmann, 2003; Patnaik, 2003). Uranium observed in these samples is dominated by contributions from the device, as evident from the relatively high $^{235}$U enrichment observed (*ibid.*). Uranium metal and UO$_2$ are generally even more refractory, with boiling points of 4000 K and 3800 K, respectively (IAEA, 2008). The maximum calculated temperature of deposition ($T_{dep}$; Table 2) has a lower temperature than the boiling point for species of element observed to be enriched at the interface, as well oxides present in the soil that were found to be depleted at the interface (*e.g.*, Al$_2$O$_3$). All the aforementioned species (FeO, CaO, U, UO$_2$, and Al$_2$O$_3$) are expected to behave as refractory species and condense out of the vapor phase at higher temperatures. The observed enrichment and depletion behavior at agglomerated fallout interfaces is therefore puzzling.

Using the calculated deposition temperature of ~2200 K from our diffusive modeling, we can now interpret the condensation behavior of species enriched or depleted at fallout interfaces (as observed in Weisz *et al.*, 2017) based on temperature-dependent vapor-pressure relationships. The vapor pressure of Al-species in oxidizing (atmospheric) conditions is roughly two orders of magnitude lower than for the Ca-species at ~2200 K, but approximately the same under reducing conditions at that temperature (Lamoreaux *et
Al₂O₃ has a much higher average concentration compared to CaO in soils presumed to be the primary precursor source material (Table 3). If any significant amount of soil was vaporized in the nuclear event, a higher concentration of Al-species in the fireball vapor would be expected in either oxidizing or reducing conditions, and thus, a higher partial pressure based on Raoult's law. In order for an excess of Ca to be present at the interface relative to Al at the calculated deposition temperature (~2200 K), a source of Ca in addition to from vaporized soil must have been present (such as a cement structure) to increase the concentration of Ca-species in the vapor. Such an addition would subsequently increase the partial pressure of Ca-species, relative to Al-species prior to formation of the interfaces, and could result in the observed enrichments. For example, rough estimates of the amount concrete needed to produce the excess Ca observed at the interface suggest a concrete to soil ratio of approximately 1:14 (see Electronic Annex 2, based on estimates of vaporized soil from Izrael, 2002) could explain these observations. Multivariate statistical approaches assessing the spatial relationships in major element species (e.g., see Fitzgerald et al., in press) may be used to test this hypothesis in future studies.

The co-location of Na₂O (relatively volatile, Walter and Giutronich, 1967) with refractory material at agglomerated fallout interfaces is at odds with current understanding of the relative volatilities of species present in the fireball after a near-surface nuclear event. Assuming equilibrium conditions at ~2200 K, the vapor pressure of CaO is expected to be more than 7 orders of magnitude lower than Na (the constituent with the highest vapor pressure of the Na-oxide species) in an oxygen-rich environment (Lamoreaux et al., 1984; Lamoreaux et al., 1987). In a reducing environment, the vapor
pressure of Ca (the constituent with the highest vapor pressure in reducing environments) is 11 orders of magnitude lower than Na, even at <1400 K. In either environment, Ca-species and Na-species would be expected to experience relative chemical fractionation, particularly given that Na₂O is more than 2-fold more abundant in the soil than CaO (Eppich et al., 2014). In contrast, in an oxygen-rich environment, the vapor pressure of Na approaches atmospheric pressure at around 2200 K (Lamoreaux et al., 1984). Co-location of Na- and Ca-species would only be possible in an oxygen-rich environment (such as theorized by Adams et al., 1960 and Miller, 1960). This effect would be enhanced in samples such as those studied here if there was substantial contribution of Ca to the vapor from sources other than local soils.

The co-location of Na and Ca enrichment bands at object interfaces resulting from oxygenated fireball conditions is in apparent contrast with recent noble gas measurements in fallout. Measurements of Xe precursor volatility indicate that, in some events, the fireball was in a reducing state at the time of system closure (Cassata et al., 2014). However, a recent XANES study of melt glass from near-surface nuclear tests suggests the cooling rate of the fireball (and the carriers entrained in the fireball) can affect the final redox state of the resultant fallout glass (Pacold et al., 2016). It is possible that the incorporation of xenon isotope precursors (the decay products of fission products) into the volume of molten fallout glasses may occur in an earlier, low fO₂ state, while the deposition layers observed in the agglomerated fallout objects in this study are the result of a later stage addition under more oxygenated fireball conditions.

While Raoult's law and studies such as those by Lamoreaux et al. (1984, 1987) can be used to estimate the vapor pressure and condensation behavior of individual species in a
multi-component vapor, these approaches are only applicable to ideal solutions. Interpretation of recent observations in fallout are further complicated when considering the effect of oxidation on a multicomponent vapor, resultant condensates, and multicomponent carrier materials in a high temperature environment. These complications are particularly evident for uranium. Uranium fractionation studies in fallout have reported both refractory and volatile behavior of uranium in post-detonation environments (Moody et al., 2014). Divergent uranium volatility is possibly attributable to the co-existence of multiple species of gaseous uranium in the fireball, each having different thermochemical properties. Species present could include U, UO, UO₂, and UO₃ among others (Grenthe et al., 1992), which have changing, temperature-dependent vapor pressures depending on oxygen fugacity (Rauh et al., 1954). Further, the interaction of uranium with other constituents in a multicomponent vapor could form numerous other complex species, each with a distinct condensation behavior.

Such complex behavior is not limited to uranium and oxygen. In vaporization experiments including multiple oxides such as those found in soils (e.g., CaO, MgO, Al₂O₃, TiO₂, and SiO₂), formation of complex gaseous oxides such as CaAlO, CaSiO₃, MgAlO, AlSiO, and CaTiO₃ has also been observed (Shornikov and Yakovlev, 2014). The formation of complex compounds could promote volatility-driven chemical fractionation for some species, and explain why in this study we observe a deposition temperature that is much lower than that predicted based on the boiling points of uranium metal or UO₂, alone (4000 K and 3800 K, respectively). Multicomponent, vapor-phase experiments with controlled oxygen environments will be necessary to determine the extent of this effect, and enable predictive generalization to fallout formation models.
4 Conclusions

The $^{235}\text{U}/^{30}\text{Si}$ ratio profiles modeled for this study are illustrative of a deposition layer of condensed species onto a molten carrier, and subsequently preserved between two agglomerated, quenched objects. Thermal transport between the fireball and molten carriers can be modeled by applying a one-dimensional diffusive model to compositional interfaces with Gaussian distributions. Results indicate that mass transport from these agglomerate interfaces occurs in less than a few seconds. This process depends on the residence time of the carrier in the fireball, as well the temperatures experienced by the molten carrier material. While these parameters are a function of fireball size to some degree, we find the deposition temperatures to be relatively insensitive to fireball yield.

By constraining the duration of mass transport based on diffusion profiles preserved at agglomerated fallout interfaces, we estimate a maximum temperature of deposition of ~2200 K. At ~2200 K, the observed co-location of Na with Ca (and other, more refractory species such as Fe and U) at some interfaces indicates that the fireball was oxygenated at the time of this surface deposition, prior to agglomeration and quenching. The comparable vapor pressure values for Ca and Al (both depleted at these types of interfaces) suggest that Ca enrichment in these interface layers originated, at least in part, from sources beyond those of vaporized near-field soils.

This study demonstrates that micro-scale fallout features preserve useful constraints on fallout formation processes and fireball time-temperature histories. Our observations also imply that oxygen availability in the fireball as a function of time may impact the speciation and relative volatility of vaporized species, and that the degree fireball oxygenation likely changes as a function of time. A more complete understanding of such
processes and their effect on resultant fallout compositions may be gained through study
of speciation of vaporized constituents under varying oxygen fugacity.

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7 Tables

Table 1

Table 2

Table 3

10. Figures

Figure 1. Top left: Optical microscope image of Sample C, a mm-scale aerodynamic fallout glass. Attached, secondary objects are labeled as C1, C2, and C3. Top right: Back-scatter electron (BSE) image of Object C1 attached to Sample C. The interface between the two objects is seen as a bright, diffuse region, indicating higher relative average atomic number in that region. The NanoSIMS isotope ratio image of $^{235}$U/$^{30}$Si is superimposed over the region where it was acquired at the interface. Bottom left: Isotope ratio image of $^{235}$U/$^{30}$Si at the interface of Object C1. The region of higher $^{235}$U/$^{30}$Si, indicative of higher $^{235}$U concentration, is seen as the white/yellow region, which is co-located with the interface. Bottom right: The $^{235}$U/$^{30}$Si ratio variation across the interface of Object C1, as acquired from the isotope ratio image along the white arrow (bottom left pane).

Figure 2. NanoSIMS ion images (left panes) and isotope ratio variation profiles (right panes) across the interface for $^{235}$U/$^{30}$Si for Objects B1, C1, and D2. The isotope ratio profiles for these interfaces were the ones best fit with a Gaussian distribution out of the sample set, with minimal variation on either side of the interface.

Figure 3. Top: BSE image of the interface between Sample D and Object D2. The interface region is very thin (<5 microns) in comparison to the larger objects. Bottom: Schematic of mass transport from an infinitesimal planar source (red) through a volume (blue) having cross sectional area A, which was used to model deposition layers as shown at Interface D2 (above).

Figure 4. (A) COMSOL 3-D mockup (see Electronic Annex 1) of aerodynamic fallout glass where two objects have fused together, where the grid scale is in millimeters. The large object is 1.5 mm in diameter, and the smaller attached object is 0.4 mm in...
diameter. (B) Wire frame of the meshed geometry, using tetrahedra from 1 micron to 100 microns, to model the geometry.

Figure 5. (A) Temperature profile of the 3-D fallout mockup acquired by finite element analysis after 1.0 s of cooling in a 1 kt fireball from 2500 K. This model incorporates conductive and radiative thermal transport with the external environment and within the object. The black arrow indicates the interface point, where the cooling rate equation of the interface was determined for the yield series. (B) Modeled cooling curves for agglomerated fallout interfaces assuming 0.1 kt, 1 kt, 10 kt, and 100 kt yields.

Figure 6. The cumulative probability distribution function of deposition times for interface B1 is shown in a 1 kt cooling environment. The blue line represents the error function fit of the dataset, which was used to derive uncertainties on the time of deposition (Table 2).

Figure 7. Modeled interface cooling rate vs. modeled fireball cooling rate, for a 1 kt fireball environment. The fireball cools to 1500K in less than 3 seconds, while the interface does not cool to 1500K until 4 seconds have elapsed.

Figure 8. Left: BSE image of Object C2 attached to Sample C. The $^{235}$U/$^{30}$Si isotope ratio image is shown superimposed over the interface. Middle: The $^{235}$U/$^{30}$Si isotope ratio is shown. The region of high $^{235}$U/$^{30}$Si ratio is shown skewed towards the larger object, indicative of faster mass-transport into the larger object vs. Object C2. Right: The $^{235}$U/$^{30}$Si ratio variation profile, as acquired from the isotope ratio image along the white arrow, illustrates this skewing, showing a sharp increase from Object C2 at the interface, and a gradual decrease from the maximum at the interface into the larger object of Sample C.

Figure 9. Temperature of deposition for each modeled interface vs. the log of the modeled yield, with $1\sigma$ uncertainties. The red line is a linear fit, from which the approximate temperature of deposition can be extrapolated for varying yields. While the fit is only applied to the data points, uncertainties in $T_{\text{dep}}$ at each yield are systematic (each is dependent on the uncertainties of the diffusivity parameters of uranium). As shown here, the estimated maximum deposition temperature is 2200 K, with maximum $1\sigma$ uncertainties of ~200 K.