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The morphologies and compositions of depleted uranium particles from an environmental case-study

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ABSTRACT

Uraniferous particles from contaminated environmental samples were analysed by scanning electron microscopy with energy dispersive X-ray analysis (SEM-EDXA) and microfocus extended X-ray absorption fine structure (μ EXAFS) spectroscopy. The particles of interest are uranium oxides, which were released into the environment by the combustion of scrap depleted uranium (DU) metal at a factory in Colonie, New York, USA. Most of the identified particles appear to have primary, 'as emitted' morphologies; some have evidence of minor dissolution, including corrosion pitting. Polycrystalline and often hollow microscopic spheres were identified, which are similar to particles produced by DU munitions impacting armoured targets. They are attributed to the autothermic oxidation of melt droplets. The compositions of the analysed spheres are dominated by UO_{2+x} with variable amounts of U_3O_8 , two of the least soluble and least bioaccessible phases of U. These particles, collected from dusts and soils, have survived more than 25 y in the terrestrial environment. This study further supports the case for using Colonie as an analogue for battlefield DU contamination.

KEYWORDS: depleted uranium, DU, uranium oxide, particles, morphology, EXAFS, SEM, environmental, mineralogy, bioaccessibility.

Introduction

Case study

NATIONAL LEAD INDUSTRIES (NLI) operated a plant in Colonie (New York, USA), from 1958–1984. The plant processed U metals (DU and some enriched uranium) and manufactured kinetic energy penetrators, counterweights and radiation shielding from depleted uranium (DU). Uranium tetrafluoride (UF_4) was reduced to metal by Mg. Scrap metal was combusted in a furnace prior to disposal as uranium oxide, which resulted in emissions of uranium oxide particulates to the environment (ATSDR, 2004). Contamination of

the suburban environment surrounding the NLI plant by DU is evident in air filters, surface soils, reservoir sediments, dusts and the urine of former employees and some residents (Dietz, 1980; Jeter and Eagleson, 1980; Arnason and Fletcher, 2003; Lo *et al.*, 2006; Lloyd *et al.*, 2008; Parrish *et al.*, 2008; Lloyd *et al.*, 2009).

From the soil concentration data of Jeter and Eagleson (1980), we estimated that at least 3.4 tonnes of U was deposited within 1 km² of the NLI plant (Parrish *et al.*, 2008) and that the distribution of contamination was controlled by prevailing winds (Lloyd *et al.*, 2008). Soils and dusts from the vicinity of the NLI plant were contaminated by the aerial deposition of anthropogenic U particulates; the vast majority of this contamination was deposited prior to 1980. From

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a sample of 115 particles, individually analysed by laser ablation-multicollector- inductively coupled plasma-mass spectrometry (LA-MC-ICP-MS), all were found to have DU isotope ratios, $n^{235}\text{U}/n^{238}\text{U} = (1.5-2.4) \times 10^{-3}$ (Lloyd *et al.*, 2009). The aim of this research is to define the present forms of contaminant U and to relate these to emission processes and their subsequent exposure in the terrestrial environment.

The primary concern for this radioactive and toxic material is inhalation exposure. The lung is the radiological 'target' for the less soluble U compounds (e.g. UO_2 and U_3O_8), the bones and kidney (also toxicological) for the more soluble compounds (e.g. UO_3) which enter the bloodstream *via* the lungs (Eidson, 1994). The Royal Society concluded that for most battlefield DU exposure scenarios, the human-health risks were low and affect a small number of people (The Royal Society, 2001, 2002). The ATSDR found that the inhalation of DU emissions from the NLI plant could have increased the risk of health effects for Colonie residents (ATSDR, 2004).

DU particulates from munitions

High velocity DU metal projectiles, which are typically an alloy of DU and 0.75 wt.% Ti, are used as armour-piercing munitions by British and American tanks and American A-10 aircraft. These DU 'kinetic energy penetrators' pierce heavy armour efficiently. Upon impact, the metal combusts and a fraction is dispersed as uranium oxide particulates (The Royal Society, 2001; Bleise *et al.*, 2003).

We aim to use the Colonie case-study as an analogue for the contamination from munitions use and to investigate the environmental fate of this controversial contaminant. The Colonie site has a relatively large contamination footprint ($\sim 100 \text{ km}^2$); the area is readily accessible and the contamination has been in the environment prior to 1984 (cf. the first reported deployment of munitions was during the 1991 Gulf War). However, the Colonie particulates were generated in a furnace that probably did not achieve the high pressures and temperatures (up to 3639 K, Patrick and Cornette, 1978) of munitions impacting armoured targets and the particles may therefore differ in composition and morphology. Their combustion may have been less heterogeneous than for munitions, which undergo an initial high energy impact and interaction with armour materials, followed by combustion or low-temp-

erature oxidation of fragments that perforate through the target, resulting in highly heterogeneous particle morphologies (Krupka *et al.*, 2009). This study addresses one of the recommendations of The Royal Society (2002) that information should be obtained on the bioavailability of DU particles. Colonie has also been proposed for health studies (e.g. Parrish *et al.*, 2008) and further information on the nature of the contamination is therefore desirable.

A brief review of the literature pertaining to the oxidation states of anthropogenic uranium oxide particles from environmental samples and from DU munitions testing is presented in Table 1. We focus on the combustible products, rather than the corrosion products of uranium. However, the origin of environmental particles is not always clear from the literature. Although each individual study is limited by small sample size, particles from environmental samples tend to be dominated by UO_2 and mixed $\text{UO}_2-\text{U}_3\text{O}_8$, but also include U_3O_8 and, rarely, uranyl species (U^{6+}). The Chernobyl particles revealed heterogeneity between rim and core, attributed to formation processes.

Aerosols from DU test-firing and combustion experiments appear primarily to be U_3O_8 . However, these studies analysed bulk samples using X-ray diffraction (XRD) techniques. In XRD, peak overlaps from U_3O_8 and U_4O_9 can mask minor amounts of UO_3 and UO_2 respectively (Krupka *et al.*, 2009). Microfocus X-ray absorption techniques (μXAS) can analyse individual particles and parts thereof, but fine particulates represented in the bulk samples are less likely to be located for analysis, potentially biasing the results. XAS is capable of resolving U_3O_8 from UO_3 .

The significance of U speciation is discussed in the next section. It is an aim of this study to determine the U speciation of particles from Colonie environmental samples and to resolve heterogeneity where possible. We used μXAS techniques, including: X-ray absorption near edge spectroscopy (XANES), which is sensitive to oxidation state; and extended X-ray absorption fine structure (EXAFS) spectroscopy, which is a probe of local atomic structure (Koningsberger and Prins, 1988).

The environmental behaviour of uranium oxides

Uraninite (hyperstoichiometric cubic/tetragonal phase UO_2 or UO_{2+x} , where $x < 0.33$) and other U^{4+} species have extremely low solubility under reducing conditions (Langmuir, 1997). In

TABLE 1. Review of uranium speciation in the combustion products of uranium metals, from environmental samples and DU munitions testing.

Sample	Analytical methodology	Oxides	Reference
Nuclear accident particles Chernobyl (1986)	μ -XRD/ μ -XANES	fire: UO_2 cores, U_2O_5 - U_3O_8 rims explosion: UO_2 cores, reduced rims	Salbu <i>et al.</i> (2001)
12 DU particles Kosovo conflict (1999)	μ -XANES (point of inflection)	UO_2 , UO_2 - U_3O_8	Salbu <i>et al.</i> (2003)
8 DU particles Kosovo conflict (1999)	μ -XANES (least squares fitting)	U^{4+} , U^{6+} - U^{6+}	Török <i>et al.</i> (2004)
7 DU particles Kuwait, Gulf War (1991)	μ -XANES (point of inflection)	DU corrosion products: UO_2 - U_3O_8 munitions fire: U^{3+} - U^{6+} (uranyl)	Salbu <i>et al.</i> (2005)
Nuclear weapons accident particles Palomares (1966) and Thule (1968)	μ -XANES	UO_2 , UO_2 - U_3O_8	Lind <i>et al.</i> (2007)
DU combustion test aerosol samples (bulk)	XRD	U_3O_8 (minor UO_2)	Elder and Tinkle (1980)
DU munitions impacting armoured targets (bulk)	XRD	U_3O_7 , U_3O_8 (minor UO_{2-x})	Mitchel and Sunder (2004)
DU munitions impacting armoured targets, aerosol samples (bulk)	XRD	$\text{U}_3\text{O}_8/\text{UO}_3$ and $\text{U}_4\text{O}_9/\text{UO}_2$ (minor $\text{UO}_{3,2}\text{H}_2\text{O}$)	Parkhurst <i>et al.</i> (2004) and Krupka <i>et al.</i> (2009)

oxidizing surface and ground waters, dissolution of UO_2 proceeds by an oxidation step, forming the significantly more soluble U^{6+} species, e.g. UO_2^{2+} and uranyl complexes (Wang and Katayama, 1982; Torrero *et al.*, 1998; Roth and Jonsson, 2008). The differences in solubility between the U^{4+} and U^{6+} species are apparent in the absorption rate classification of uranium oxides for dose assessment from inhalation exposure. Ansoberlo *et al.* (2002) classified UO_2 and U_3O_8 as slow, Type S (ICRP, 1995), with dissolution half-lives in simulated lung fluid of at least 700 days, U_3O_8 dissolving more rapidly than UO_2 . In contrast, UO_3 has a dissolution half-life of less than 10 days and is classified as fast, Type F.

The initial rapid dissolution rates seen in *in vitro* lung fluid experiments (e.g. Mitchel and Sunder, 2004; Parkhurst *et al.*, 2004; Guilmette and Cheng, 2009), may be accounted for by mixtures of particle sizes, morphologies and oxide phases including surface products. Depleted uranium aerosols generated from munitions impacting armoured targets had variable and complex solubility in simulated extracellular fluids, with dissolution behaviour similar to either Type M (intermediate rate) or Type S (Parkhurst *et al.*, 2004; Guilmette and Cheng, 2009). Thus, the degree of oxidation and the process of oxidation are significant to both the environmental fate and bioaccessibility of uranium oxide contamination. It should be noted however, that these experiments do not simulate the action of macrophage lysosomes, which convert U_3O_8 to insoluble phosphate phases *in vivo* (Berry *et al.*, 1997).

Stoichiometric UO_2 oxidizes readily in air and fine powders can behave pyrophorically. At environmental temperatures, thin films (a few nm thick) of higher oxides form on UO_2 in air; UO_3 is thermodynamically favoured, but this reaction is limited by oxygen ion diffusion (McEachern and Taylor, 1998). Surface uranyl (UO_2^{2+}) ions are observed from the oxidation of hyperstoichiometric UO_2 (UO_{2+x}) in moist air at 353 K (Schueneman *et al.*, 2003). Polycrystalline $\text{UO}_{2.05}$ has also been observed to oxidize partially, over 15 y in ambient conditions, to $\text{UO}_3 \cdot 2\text{H}_2\text{O}$ (metaschoepite) (Wadsten, 1977).

The uranium dioxide fluorite-type cubic lattice and its derivatives (UO_{2+x}) accommodate interstitial oxygen atoms in the range UO_2 – $\text{UO}_{2.33}$ / β - U_3O_7 ; higher oxides (U_3O_8 – UO_3) adopt an orthorhombic lattice with lower density (Allen and Tempest, 1986). At elevated temperatures, bulk oxidation of UO_{2+x} can occur, including

U_3O_8 formation at temperatures greater than about 523 K (McEachern and Taylor, 1998). Uraninite (UO_{2+x}) is the most common U ore mineral, but re-crystallization to orthorhombic U_3O_8 has never been reported in nature, demonstrating the environmental stability of this mineral (Finch and Ewing, 1992). Thus, U_3O_8 and higher oxides will not be formed in significant quantities from UO_{2+x} in ambient air, but could have formed in the NLI conversion furnace. The rate of U_3O_8 formation on UO_2 powders is slow, forming as a major product at 533 K in around 25 h (references in McEachern and Taylor, 1998).

Anderson *et al.* (1955) compared the oxidized thin surface films on UO_2 powders to those forming at low temperatures on other metals. Passive surface oxide films (nm thick) form on metals such as Al, protecting the bulk metal from further oxidation; however these films are susceptible to corrosion pitting. This process is autocatalytic in the presence of water and a strong anion, e.g. Cl^- (Frankel, 1998). This process might therefore promote oxidation and dissolution of uranium dioxide.

Methodology

Samples

Particles of interest were concentrated from contaminated dust and soil samples collected from the vicinity of the former NLI site in Colonie. The dust samples for μXAS were collected from a covered site at ground level, which has accumulated windblown material over several decades (it is possible that these samples were occasionally saturated by rainwater). This site afforded a large quantity of relatively concentrated material ($385 \pm 33 \mu\text{g g}^{-1}$ U, cf. natural U concentrations in Colonie soils at $\sim 1 \mu\text{g g}^{-1}$). Other dry dust samples from residential properties were collected by brushing or dry wiping material into clean polystyrene tubes. Soil samples were collected by hand-auger from the surface to a depth of 15 cm.

Sample preparation

Sample preparation methodology is detailed in Lloyd *et al.* (2009) and summarized here. Soil samples were dried at between 40 and 60°C and sieved to <2 mm. Dense grains and particulates, including uranium oxides greater than approximately 20 μm diameter, were concentrated by dense liquid separation (using di-iodomethane,

$D = 3.3 \text{ g cm}^{-3}$). Magnetic minerals, iron oxides and some zircons were removed by magnetic barrier separation (Frantz LB-1). This methodology is rapid when compared to fission-track or sample splitting techniques.

For electron microscopy, both raw sample and concentrates were mounted by dabbing the surface of a carbon adhesive disc onto the sample material and lightly tapping to remove loose grains.

For XAS, an individual particle approach was required. From the dense concentrates, particles with anthropogenic appearance, including spherical particles, typically 20–80 μm in diameter and with a glassy or metallic lustre, were picked under an optical microscope using fine tweezers. Larger, frosted and rounded quartz grains had previously been removed by density separation. The remaining natural dense minerals grains were typically sub-angular, with irregular or crystalline habit (including detrital zircons, garnet, rutile, etc.). Picking was performed in a Petri dish with the grains submerged in ethanol, the grains of interest were transferred by pipette to a clean dish and the ethanol evaporated.

The particles of interest were then transferred by tweezers to a low-tack adhesive mount. For this we used, as a substrate, *Glue Dot Repo*[™] (Keighley, UK), a proprietary craft material that appears clean and from which particles can easily be removed without visible residue. The mounts were then examined by SEM-EDXA. Uraniferous grains were identified by the presence of U- $M\alpha$ X-ray peaks.

Of several thousand picked particles, fewer than one in ten comprised U, with most of the rest comprising Pb, Sn and/or silica. The uraniferous particles are typically opaque, dark grey with a dull metallic lustre; they tend to be fragile and some are hollow shells. The uraniferous particles were then transferred, embedded in epoxy resin and polished to reveal their cross-sections. Images from the sample preparation steps can be found in Appendix 2.7. Appendices are deposited with the Principal Editor of *Mineralogical Magazine* and are available from: www.minersoc.org/pages/e_journals/dep_mat_mm.html.

X-ray absorption spectroscopy (XAS)

Standards

We are not aware of any commercially available stoichiometric uranium oxide standard and it appears that many chemical companies

have stopped stocking these compounds. Three uranium oxide compounds were purchased from IBI Labs (Boca Raton, Florida, USA): UO_2 , U_3O_8 and $\gamma\text{-UO}_3$.

XRD revealed that none of these powders were pure. The U_3O_8 was mixed with $\text{UO}_3 \cdot 2\text{H}_2\text{O}$ (metaschoepite), $\text{UO}_3 \cdot 0.8\text{H}_2\text{O}$ (dehydrated schoepite) and Ag_2S (acanthite), but we were able to pick black U_3O_8 grains from this material. Contamination of UO_2 by $\text{UO}_3 \cdot 0.8\text{H}_2\text{O}$ (dehydrated schoepite) was insignificant. The $\gamma\text{-UO}_3$ was mixed with a significant quantity of another U^{6+} compound, $\text{UO}_3 \cdot 0.8\text{H}_2\text{O}$. Further information on the XRD analyses can be found in Appendix 1.5. The compounds were ground in an agate pestle and mortar; approximately 20 mg U equivalent were mixed with boron nitride (BN) powder and compressed into 8 mm diameter pellets.

Experimental

XAS was performed at the microfocus spectroscopy beamline I18 of The Diamond Light Source (Harwell, UK), a third generation electron synchrotron (3 GeV, 250 mA), described in Mosselmans *et al.* (2008). The X-ray beam diameter at the sample position measured 3.5 μm .

The experimental set-up is shown in Fig. 1. Standards were measured in transmission mode and the samples by fluorescence (measured perpendicular to the excitation beam). Similar information can be derived from the two analysis modes. The standards were measured once each, twice for U_3O_8 (with similar results). The spectra are supported by theoretical modelling. For each sample particle, three or four separate spot analyses were measured in duplicate using the same beam position for each duplicate measurement. No difference was apparent between duplicate spectra that could be attributed to oxidation.

X-ray absorption spectra were collected using a Si(111) double crystal monochromator scanned over the range 17.00–17.35 keV, crossing the U- L_{III} absorption edge in 0.5 eV steps, counting each step for 1 s, increasing to 2 eV steps and 4 s for higher energies. In the analyses of the spectra, the edge positions were calculated as the point of inflection (peak of first derivative of $\mu(E)$, after low-pass Fourier transform filter).

Microfocus extended X-ray absorption fine structure (μEXAFS), $\chi(k)$ spectra were isolated using *PySpline* (Tenderholt *et al.*, 2007), by least squares fitting of quadratic splines and optimization of the Fourier transform (radial function). Extended X-ray absorption fine structure modelling from

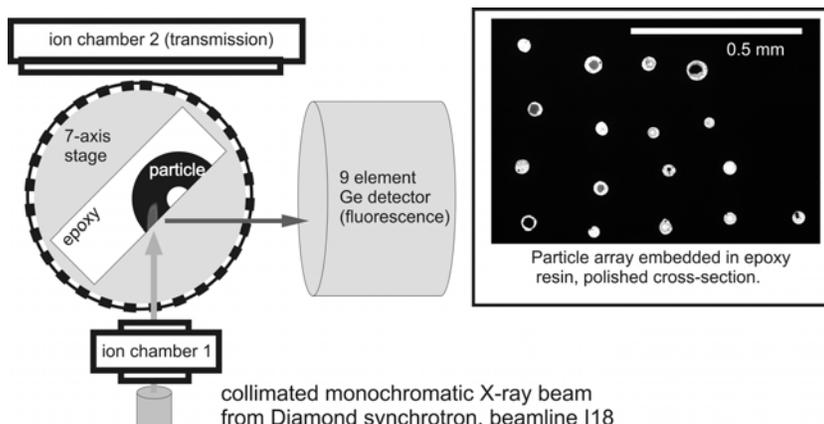


FIG. 1. Diagram of the experimental set-up for XAS, standards were measured in transmission mode, samples by fluorescence. SEM image of particle array (right).

crystallographic data was performed using *DL_EXCURV* (Tomic *et al.*, 2005), achieving reasonable fits to the standard spectra (to $k = 9.5 \text{ \AA}^{-1}$) from 3 scattering shells (2 for UO_3), including multiple scattering paths (see Fig. 2).

Scanning electron microscopy (SEM-EDXA)

Two SEMs were used to investigate raw dust samples, dense concentrates from dusts and soils and picked uranium oxide spheres: (1) a Hitachi S-3600N ‘environmental’ SEM fitted with an

Oxford Instruments Inca X-sight; and (2) an FEI Sirion 200 field emission SEM fitted with a Princeton Gamma Tech. ‘Spirit’ X-ray analyser. Energy dispersive X-ray spectrometers cannot quantify oxygen and it was therefore not possible to distinguish the different uranium oxides phases. The environmental SEM, operating at $P = 20 \text{ Pa}$, allowed uncoated specimens to be imaged using backscattered electron (BSE) detectors; this mode facilitates detection of heavy elements such as U. Carbon coating and high vacuum were used for secondary electron (SE) imaging. Accelerating

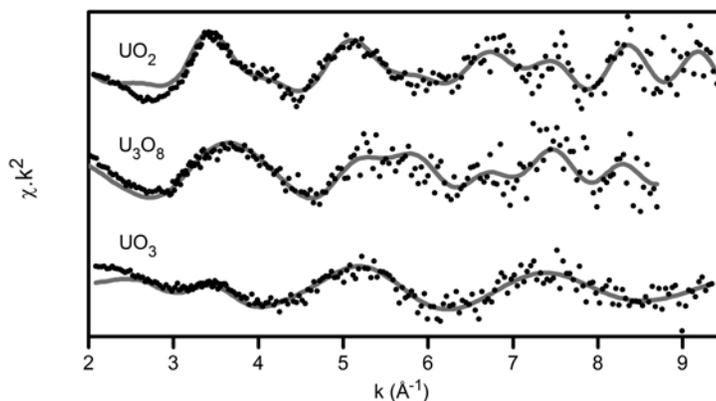


FIG. 2. EXAFS spectra from standards: experimental data points (dots) and theoretical models (lines). The models achieve reasonable fits from 3 scattering shells (2 for UO_3) and are based on crystallographic data from ICSD (Fletcher *et al.*, 1996). The second dominant oscillations, peaking in the region $k = 3-4 \text{ \AA}^{-1}$, are distinct for each standard. For UO_2 , contributions from the first oxygen and uranium scattering shells create a distinctive asymmetric second peak in this region. It should be noted that the amplitude of EXAFS in measured absorption spectra decreases with k value. Therefore, they are amplified by k^2 , but noise becomes an inherent issue at higher k values.

voltages of 15–30 kV were used; lower accelerating voltages improve spatial resolution, but higher accelerating voltage improves X-ray detection.

Results

SEM-EDXA

Composition

The majority of the EDXA spectra from the uraniferous particles analysed were dominated by the U- $M\alpha$ peak (3.17 keV), an O- K peak and also a C- K peak generated from the mounting substrates. This was almost exclusively true of 'clean' areas from uraniferous spheres. Aluminium and Si peaks were commonly associated with surface-adhering clays, appearing as dark cloudy regions in BSE mode and translucent platy regions in SE mode. Other common elements, frequently identified as surface contamination, included Mg, Fe, Na, Mn, Ca, K, Cl, S, and less commonly Cu and P. Peaks from Ti were, on occasions, also identified; however, the Ti concentration in the DU alloy, at ~0.75 wt.%, is close to the limit of detection for this method. Molybdenum and Nb were not detected, although these elements were used in some DU alloys instead of Ti in an attempt to improve mechanical properties and corrosion resistance (Hopson *et al.*, 1973).

Size

Uraniferous particles from raw samples were identified with geometric diameters in the range 0.5–150 μm (approximate unimodal log-normal particle size distribution, coarse particle size-range; see Appendix 2.8 for histogram). The threshold for respirable particulate matter (PM_{2.5}, particulate matter less than 2.5 μm aerodynamic equivalent diameter) is 0.8 μm for UO₂ ($D = 10.96 \text{ g cm}^{-3}$). Particle size distributions were not accurately determined, because location by SEM becomes increasingly difficult for smaller particulates. Particles of interest are scarce in raw samples and concentrates are inherently biased because fine particulates <~20 μm diameter do not settle readily in dense liquids. Importantly, it was noted that the particles are often brittle and easily broken into smaller fragments, some of which would then be inhalable.

Morphology

Figure 3 presents a selection of 18 SEM micrographs of uraniferous particles identified

from environmental dust and soil samples; their morphologies are described in the following text. Additional micrographs, including all of the identified uraniferous spheres, with the cross-sections of those analysed by XAS, are presented in Appendix 2.

Figure 3a shows a well preserved uranium oxide sphere from a dust sample; the surface is split and there is some evidence of minor pitting on the surface (Fig. 3b). Based on their geometry, we interpret the cavities in the surface of spheres Fig. 3c,d (both from soil samples) as possible evidence of corrosion pitting. Corrosion pitting is a process to which uranium oxides, for reasons previously discussed, are likely to be susceptible in the environment. We also considered the etching of alpha recoil damage from ²³⁸U decay and although the distribution of these cavities is compatible with this idea, UO₂ recovers from this type of damage (Matzke, 1999). The amount of corrosion from these and other spheres appears minor (a few percent).

Some of the spheres have tails, consistent with mid-air solidification from a melt. Many are hollow (Fig. 3f,g), or include cavities (see Appendix 2.3), the formation of which is discussed in the following sub-section. The interior of the cavity shown in Fig. 3g contains square tabular crystals, but the spheres more typically comprise 1–2 μm diameter equiaxial crystals as in Fig. 3d, but sometimes as coarse as 12 μm in diameter as is shown in Fig. 3h. Some of the cross-sections reveal coarser crystals towards their centres (see Appendix 2.3).

Patrick and Cornette (1978) observed inter-connecting concave plates across the surface of uranium oxide spheres from DU munitions impacting armoured targets and interpreted their formation as melt-freezing from multiple sites across their surface. Similar platy surfaces are seen in Fig. 3h,i. The sutured platy texture in Fig. 3h is strikingly similar to that presented in fig. 7b of Krupka *et al.* (2009), but the size of particle in Fig. 3h is >5 times larger.

Some of the non-spherical particles are comprised of agglomerated 1–2 μm diameter uraniferous grains. Triple junctions between these are shown in Fig. 3j. This texture could have been created by compression of aggregates in the furnace grate, under the weight of other material. Alternatively, the texture may have been formed by powder metallurgy type processes at NLI, but it is distinct from sintered UO₂ fuel (e.g. in Kashparov *et al.*, 2004). Non-compacted

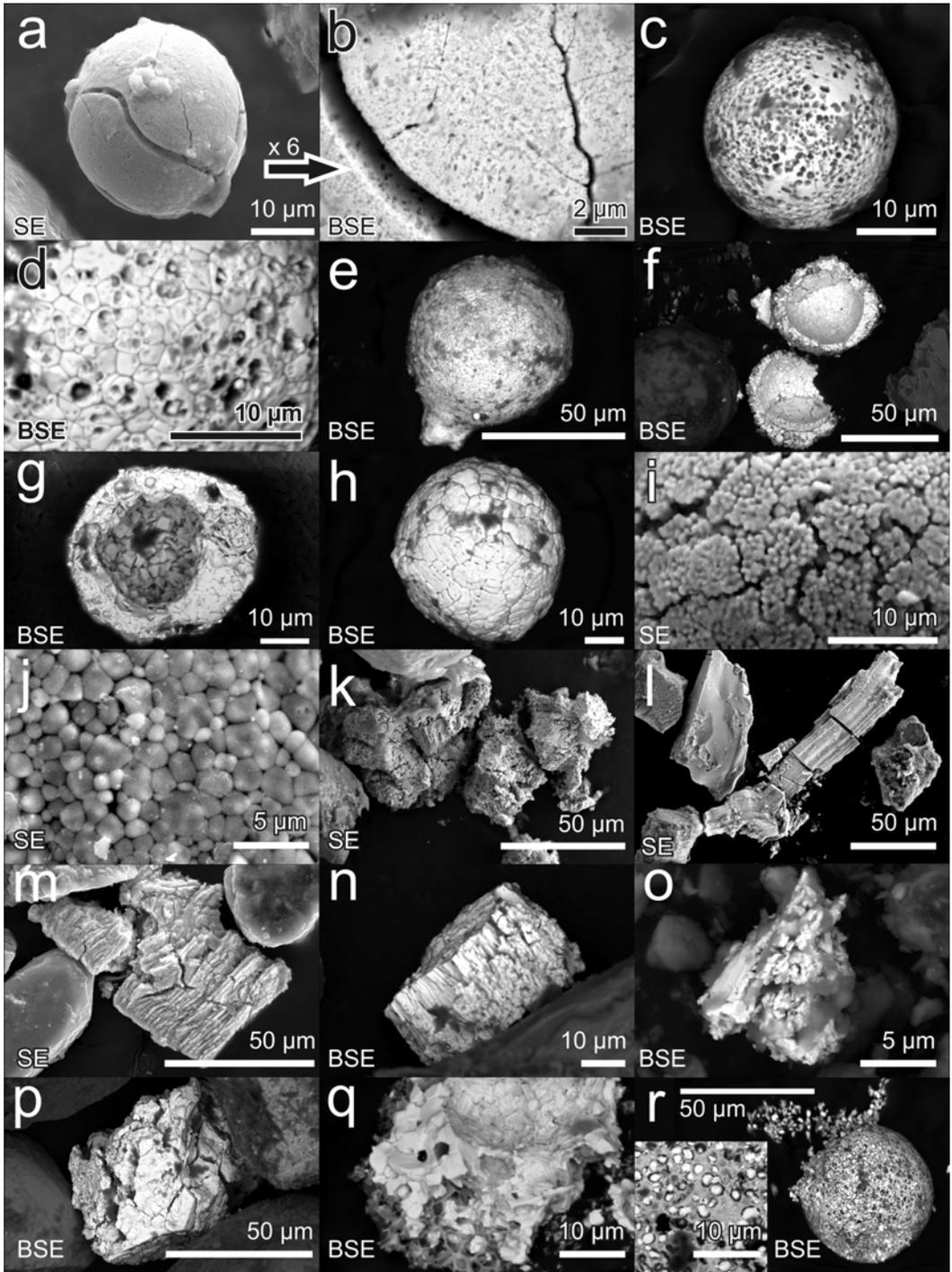


FIG. 3. SEM images of uraniferous particles from dust and soil samples, showing a range of primary morphologies and textures, which are discussed in the text. Images from soils samples are as follows: *c*, *d*, *k*, *n*, *q* and *r*.

aggregates of μm -scale diameter particulates are also seen (Appendix 2.5), similar to those from Chernobyl emissions (Salbu *et al.*, 1994). Fluffy aggregates of fine particulates are reasonably common in the samples (Fig. 3k and Appendix 2.5), and may have been produced by vapour condensation, nucleation and coagulation of particulates in the NLI furnace.

Morphologies that resemble metal shavings have been observed. Fig. 3l shows a small uraniumiferous rod that has fractured during sample preparation. This brittle behaviour suggests that it is oxidized throughout. The foliated texture displayed in Fig. 3m is typical of the combustion of DU metal ammunition between 973–1173 K (Elder and Tinkle, 1980).

In addition to spheres, the appendices in Parkhurst *et al.* (2004) include SEM micrographs of aggregates and some bladed crystal textures similar to Fig. 3n (specifically fig. D.2, or fig. 4 in Krupka *et al.*, 2009). A mixed morphology, partly ordered and polycrystalline, partly a disordered aggregate, similar to Fig. 3o, is also presented there (also in fig. 6, Krupka *et al.*, 2009).

The block of uranium oxide in image Fig. 3p shows multiple fractures, similar to expansion textures resulting from the oxidation of UO_2 to U_3O_8 (McEachern and Taylor, 1998), which could have occurred in the furnace environment. Only one such example was identified.

An unusual texture of DU oxide (+Ti) on an Al/alumina ‘honeycomb’ mesh ($\pm\text{Na}$) in image Fig. 3q, may have been formed by the partial dissolution (in a wet soil environment) of a U-Al liquid phase sintered product, or possibly U precipitation on a refractory material. Alternatively, it is similar to catalysts patented by Mabilon *et al.* (1991) but on a microscopic scale, which may have been an experimental product of NLI. Figure 3r shows a sphere that comprises $\sim 60\%$ uranium oxide crystals ($0.3\text{--}3\ \mu\text{m}$ diameter) in an Fe or Fe-oxide matrix.

More than 100 uranium oxide spheres were identified in the $20\text{--}64\ \mu\text{m}$ geometric diameter range (median $37\ \mu\text{m}$, approximate unimodal normal particle size distribution, see Appendix 2.8 for histogram). The concentration techniques employed limit this size range, especially for the lower end. These spheres are typically polycrystalline with equiaxial grains, $\sim 1\ \mu\text{m}$ diameter (estimated size range $0.3\text{--}12\ \mu\text{m}$).

Of those sectioned ($n = 45$), 42% were hollow and another 42% included cavities; only 16%

appeared solid. Of those sectioned, 60% , appeared to comprise U and O only. Minor EDXA peaks from Ti were detected in 27% of the remainder, Al in 20% and other elements in only 9% (LoD $\sim 1\ \text{wt.}\%$). Analysis of the cleaned cross-sections avoided the surface contaminants seen on the whole particles.

Formation of uranium oxide spheres

Spherical particles were deliberately picked for the XAS analyses, because they can be recognized under an optical microscope. This distinctive morphology is observed from the debris of DU munitions impacting with armoured targets (dominant morphology, Patrick and Cornette, 1978; common morphology, Parkhurst *et al.*, 2004; Krupka *et al.*, 2009) and less commonly in contaminated dusts and soils from the Colonie case-study. The coarse size of these spheres distinguishes them from the $1\text{--}2\ \mu\text{m}$ diameter spherical uraniumiferous particles formed by the oxidation and hydrolysis of UF_6 escaping from enrichment plants, which are the focus of nuclear forensic analyses (Stebelkov, 2005; Kips *et al.*, 2007).

A number of experimental studies have produced similar spheres. Jones *et al.* (1964) produced UO_2 microspheres by passing metal-oxide through an inductively coupled plasma torch (stoichiometric UO_2 microspheres $<50\ \mu\text{m}$ diameter were red in colour, some of the spheres were hollow). Surya Narayana *et al.* (1994) electrically heated UO_2 pellets to a peak temperature of $3773\ \text{K}$, producing aggregates of fine U_3O_8 particulates (attributed to vapour condensation) as well as larger low-solubility UO_2 spheres ($\sim 4\ \mu\text{m}$ diameter). Carter and Stewart (1970) produced Pu and U spheres in the $0.1\text{--}1\ \text{mm}$ range, using exploding metal wire and freefall droplets (melted and ignited at $933\ \text{K}$). They displayed a range of colours (white, yellow, orange, brown, black) and textures (reticulation, dimpling, striations, glassy). Sparks from shattering freefall droplets produced spheres, often hollow. This was interpreted as rapid volatilization and emission of U from combusting molten metal/oxide droplets.

Martz and Hashke (1998) present a conceptual model (supported by theoretical modelling and experimental data) for the combustive heating of Pu droplets. Following melting and ignition, this proceeds by autothermic oxidation and achieves very high internal temperatures sufficient to

volatilize and vent Pu, leaving fragmented and hollow PuO₂ shells. Uranium is also a pyrophoric material and UO₂ has a similar heat of formation as PuO₂ and might be expected to behave in a similar way.

Peak burning temperatures for small chunks of U metal in air reach 1773 K (Baker Jr *et al.*, 1966), exceeding the U melting point of 1405 K (Katz and Seaborg, 1957). We propose that the observed hollow uranium oxide spheres were formed by the ejection of small liquid-metal droplets, the temperatures of which were much higher than the U ignition temperature of 563–973 K (Baker Jr *et al.*, 1966). Autothermic oxidation raised their internal temperature, sufficient in many instances to volatilize and vent the contents (4091 K for U metal, Katz and Seaborg, 1957; 3815 K for uranium dioxide, INSC, 2008). This process would be observed as bright sparks spitting from the furnace and sometimes exploding. Presumably, the vapour condensed and nucleated to form ultrafine particulates and agglomerates. The stability of U₃O₈ was exceeded (1878 K, Taylor, 2005); if cooled quickly, UO_{2+x} is the expected phase (freezing at ~3120 K, INSC, 2008), but if held at intermediate temperatures this may oxidize further.

Powder metallurgy is a processing technology, commonly used to produce complex shaped metal articles directly, by compressing and sintering metal powders (German, 1994). The extreme reactivity of U metal may appear to make this unattractive. However, U metal powders have been processed by reduction of oxides and hydride-dehydride conversion (Bellamy and Buddery, 1952; Clark *et al.*, 1998). A contemporary account of U metallurgy is given in Meerson (1960).

A few of the particles identified are comprised of μm diameter uranium oxide grains with triple-junctions, a texture consistent with compressed, but not fully sintered powders (Fig. 3j). The texture in Fig. 3q could be explained as dissolution of crystalline uranium oxides from a liquid-phase sintered powder, exposing a second alumina phase.

There is some evidence that U powder metallurgy, which can produce uranium oxide spheres, may have been employed at NLI. However, the observed cavities and the size range of the spheres are not consistent with the powder metallurgy techniques typically used for U. There is strong evidence that the spheres were produced by oxidation of melt droplets.

Summary of SEM work

Electron microscopy reveals a range of morphologies and textures. Many of the uranium particles are polycrystalline and some are spherical. The uranium oxide spheres are attributed to a specific process, i.e. the autothermic oxidation of melt droplets. Similar spheres are formed by DU munitions impacting armoured targets. All of the particles presented in Fig. 3 and most of those identified by this study have primary morphologies, attributed to specific processes at NLI. Some of the particles show evidence of minor dissolution, including a few with evidence of corrosion pitting, a process that enhances oxidation and dissolution. Readily identifiable evidence of secondary particles, precipitates of U, in these samples (e.g. schoepite/metaschoepite in Appendix 2.5) is scarce.

In summary, electron microscopy reveals that dust and soil samples from Colonie are contaminated by primary uranium oxide particulates and that these have survived more than 25 y of exposure in the terrestrial environment.

μXAS

μXANES

μXANES for the standards showed the expected increase in edge position (point of inflection) for higher oxidation states, presented in Appendix 1.4. However, the estimates for the samples were typically less than the UO₂ standard and do not appear reliable.

μEXAFS

μEXAFS spectra were isolated for each point analysis, where possible from the average of replicate absorption profiles. To correct for the variable edge estimates used, the μEXAFS spectra were re-aligned for the first peak to the UO₂ standard ($k = 1.39$), *via* energy space, $\mu(\text{E})$. The μEXAFS are presented as k -squared weighted χ against k , $\chi k^2(k)$, in Figs 2 and 4 (and Appendix 1.2). Theoretical modelling of the standard spectra produced reasonable fits for 2 or 3 scattering shells, including multiple scattering paths (Fig. 2).

This study focuses on the second dominant oscillation, because the first oscillation includes the ‘white-line’ and is overly sensitive to spline fitting, and the data are noisy for the third and subsequent oscillations. For UO₂, the second

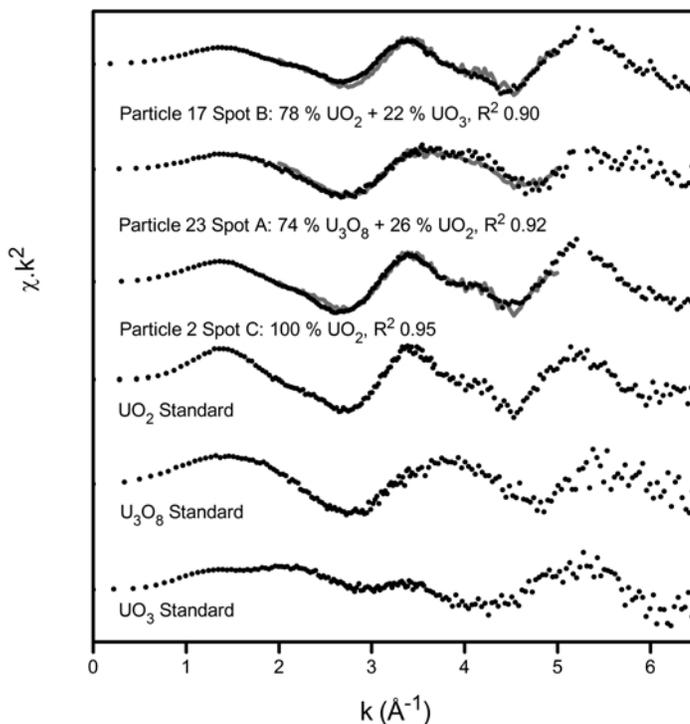


FIG. 4. μ EXAFS spectra for 3 standards and 3 selected sample spectra from the dust sample. Least-squares fitting of the standards to the sample spectra achieved good adjusted- R^2 values (>0.75 , adjusted for degrees of freedom). Fitting parameter uncertainties $\sim \pm 10\%$ for these spectra.

dominant oscillation has a pronounced asymmetric shape and can be approximated by the contributions from the first O and U shells. In contrast, the second oscillation for U_3O_8 is approximately symmetrical and slightly extended (from a closer O shell). The ' UO_3 ' spectrum is characterized by a distinctive 'shoulder' on the first peak, similar to that modelled by multiple scattering along a uranyl group (Hudson *et al.*, 1995). We applied linear combination least-squares fitting, using the three standard spectra, to each of the sample spectra, in the region $k = 2-5 \text{ \AA}^{-1}$, which covers these characteristic features.

Three selected sample spectra are compared with the standards in Fig. 4, the complete set of 42 sample spectra can be found in Appendix 1. The compositions from the spot analyses are presented in Fig. 5.

By using a microfocus beamline, it was possible to analyse different parts of individual particles, but no clear differences in composition

between rim and core were observed. With a 3.5 \mu m beam, it was not expected to detect thin surface films of higher oxides. The spatial resolution of the spot analyses averages across several crystals and grain boundaries within the polycrystalline particles. Due to the sample geometry in our experiments, it would not be possible to create a symmetrical cross-sectional profile or map from individual particles, as the leading edge is shielded by the body of the particle. Furthermore, when the edge of the particle is approached, absorption is minimized and the spectra become increasingly noisy. Physical rotation of the particle, particle sectioning and longer counting times for edge analyses would be required to overcome these issues.

Discussion

Osán *et al.* (1997) utilized a least squares fitting approach for the XANES (for As, to 40 eV above

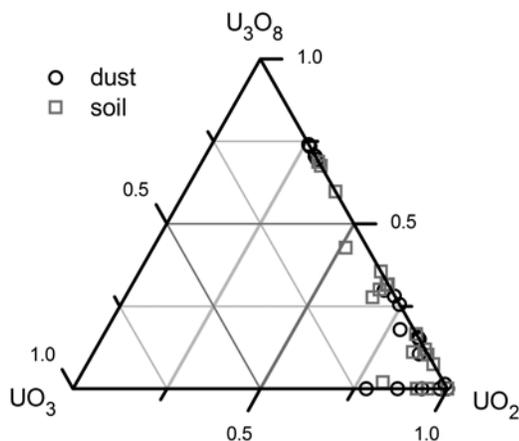


FIG. 5. Ternary diagram of the estimated compositions of microscopic uranium oxide spheres from μ EXAFS spot analyses. The compositions are dominated by UO_2 , with variable amounts of U_3O_8 . Fitting parameter uncertainties are typically ± 5 – 15% of total. UO_3 is only significant (2σ) for 3 spectra. Minor components, less than 10%, should be treated with caution. Spectra from 7 soil grains and 7 dust grains show a similar distribution of compositions. The fitting data are tabulated in Appendix 1.3.

the K -edge), fitting white-line, ‘multiple-scattering’ and edge curves to the spectra. They argued that since the white-line overlaps the true absorption edge, it is not sufficient to study this alone. Török *et al.* (2004) argued that this method is superior to the inflection points measured by Salbu *et al.* (2003).

The edge positions for our data did not prove to be reliable indicators of composition. Whether this is due to instrumental drift or some other factor is uncertain. Typical EXAFS analyses span several oscillations to higher k values and utilize the radial function to resolve contributions from individual scattering shells. The amplitude of EXAFS oscillations diminishes towards higher k values; noise therefore becomes an inherent issue. This is especially true for microfocus spectroscopy, which excites a small sample volume with a reduced X-ray intensity. Long counting times would be required to improve spectra quality, but this would limit the number of samples analysed, further compromising representativity. Therefore, sample spectra were only acquired to 7 \AA^{-1} .

This study employed an alternative strategy, least-squares fitting for a limited portion of the μ EXAFS spectra, including the second

oscillation and the uranyl shoulder of the UO_2 standard, in the region $k = 2$ – 5 \AA^{-1} . Adjusted R^2 values of ~ 0.9 and examination of the residuals, suggest that the fits are generally good. The uncertainty of the fitting parameters is typically in the range of ± 5 – 15% , precluding detailed comparisons between individual spot analyses. On a generalized and qualitative basis, the spot analyses are consistent across individual spheres.

UO_2 and U_3O_8 oxides are the most commonly reported combustive products of DU munitions in environmental samples (Table 1) and the common phases identified for these samples. This study found a dominance of UO_2 , with variable amounts of U_3O_8 . The model of autothermic oxidation and venting from melt droplets predicts core temperatures that exceed the stability of U_3O_8 , freezing as UO_2 , which may then (slowly) re-oxidize to U_3O_8 at intermediate temperatures. These data are compatible with this model.

It should be noted that these μ EXAFS spectra and the cited XAS studies, do not resolve stoichiometric UO_2 from the more than likely hyperstoichiometric uranium oxides and it would be preferable to state UO_{2+x} . Allen *et al.* (1985) and Jones *et al.* (1986) demonstrated the subtle differences in the EXAFS spectra of the cubic uranium oxides (UO_2 , U_4O_9 and $\beta\text{-U}_3\text{O}_7$); resolving these species from each other for environmental particles is probably beyond the scope of μ XAS.

Uranyl species, represented by the UO_3 standard, appear to be rare in these spheres. In contrast, uraniferous particles analysed in a core sample from a reservoir sediment (wet environment), appear to include metaschoepite (Arnason *et al.*, 2008). These reservoir sediments accumulated U compared to nearby soils and it appears likely that any uranyl species precipitated from watershed runoff, which includes effluent discharged from the NLI site.

Particulates from DU munitions impacting armour, sampled directly from aerosol and including morphologically similar spheres, are predominantly U_3O_8 and U_4O_9 in composition with no UO_2 detected by XRD (Parkhurst *et al.*, 2004; Krupka *et al.*, 2009). However, in XRD, there are spectral overlaps between U_3O_8 and UO_3 and also between U_4O_9 and UO_2 , limiting the detection of minor UO_3 and UO_2 (Krupka *et al.*, 2009). Mitchell and Sunder (2004) identified U_3O_7 as a common phase from DU munitions impacting armoured targets, along with U_3O_8 and minor

UO_{2+x}. As discussed previously, the cubic uranium oxide phases are also difficult to resolve for environmental particle samples using μ XAS. A discussion of alternative analytical techniques for U speciation is beyond the scope of this paper, but XPS (e.g. Schueneman *et al.*, 2003) and μ -Raman spectroscopy (e.g. Allen *et al.*, 1987) could be considered for future studies of this material.

The apparent differences in compositions for the DU munitions aerosol may be due to the selection of a specific morphology and size-range for this study and the inclusion of others in the bulk aerosol samples. The UO₂ rich particles are also more likely to survive environmental exposure intact, to the point of selective picking for analysis.

This study, as with those of Török *et al.* (2004) and Salbu *et al.* (2003), analysed a limited number of particles, which may not be fully representative of the environmental samples. We also acknowledge that these particles were selected by morphology from a specific size-range. It is therefore not necessarily appropriate to extrapolate these findings to respirable particulates. However, the continued excretion of anthropogenic isotope ratios by workers and some residents, more than 20 y after exposure (Parrish *et al.*, 2008), suggests that the inhaled particulates were also low-solubility phases (e.g. UO₂ and/or U₃O₈).

Conclusions

This initial study of the Colonie particles shows that mixed UO_{2+x} and U₃O₈ micro-spheres survive in the terrestrial environment (soils and dusts) for at least 25 y. The U from these low-solubility phases, dominated by U⁴⁺, is less bioaccessible and less mobile than uranyl species (e.g. UO₃). Higher solubility, uranyl species (U⁶⁺) are a rare and minor component of the analysed particles.

A range of primary particle morphologies, as emitted from NLI, have been identified and survive to the present time. The morphologies of the contaminant uranium particles include microscopic uranium oxide spheres that are similar to those produced from DU munitions impacting armoured targets. This further supports the case for using Colonie as a realistic analogue for battlefield contamination by DU. Morphological investigation and compositional analyses of uranium fine particulates in these samples are recommended for further work.

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Simon Chenery and Simon Kemp publish with the permission of the director of the British Geological Survey.

Appendices (online deposited material)

Appendix 1 – XAS spectra, fitting data and XRD of standards

Appendix 2 – Supplementary SEM images

Available from: www.minersoc.org/pages/e_journals/dep_mat_mm.html

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