An aerosol particle containing enriched uranium encountered in the remote upper troposphere

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ABSTRACT

We describe a submicron aerosol particle sampled at an altitude of 7 km near the Aleutian Islands that contained a small percentage of enriched uranium oxide. ^{235}U was 3.1 ± 0.5% of ^{238}U. During twenty years of aircraft sampling of millions of particles in the global atmosphere, we have rarely encountered a particle with a similarly high content of ^{238}U and never a particle with enriched ^{235}U. The bulk of the particle consisted of material consistent with combustion of heavy fuel oil. Analysis of wind trajectories and particle dispersion model results show that the particle could have originated from a variety of areas across Asia. The source of such a particle is unclear, and the particle is described here in case it indicates a novel source where enriched uranium was dispersed.

1. Introduction

Aerosol particles can travel great distances in the atmosphere, so any sampling of such a particle represents the possibility of dispersal of uranium into the environment. Particulate matter containing uranium can originate from sources such as combustion of coals with trace uranium, windblown crustal material, and mining and processing of ores, whether it be for the uranium itself or other minerals such as rare earths and phosphate (Hamilton, 1970; Tadmor, 1986; Yunoki et al., 1995).

Natural uranium contains about 99.3% ^{238}U (half-life 4.468×10^9 yr), 0.7% ^{235}U (half-life 7.04×10^8 yr), and 0.0057% ^{234}U (half-life 2.46×10^5 yr). Aerosol particles containing uranium enriched in ^{235}U are definitely not from a natural source. Releases of enriched uranium and other radionuclides into the atmosphere have been reviewed by Salbu and Lind (2011). Besides major single releases such as the Chernobyl reactor failure or the burnup of the Cosmos satellite reactors (Krey et al., 1979; Leifer et al., 1987), longer-term sources of uranium such as windblown dust from nuclear test sites have been postulated to increase the ^{235}U content of atmospheric uranium (Kikiwada et al., 2009). Apart from isolated events, most of the uranium in the remote atmosphere is not enriched. Even during nuclear testing in the early 1960s, fallout increased $^{235}U/^{238}U$ in alpine ice from about 0.7% to about 0.8% (Warneke et al., 2002), so enriched uranium was a small fraction of total uranium.

Measurements of uranium in the atmosphere have generally been made with bulk filter samples that can process a large amount of air for detection of very low concentrations. Measurements of single particles can add important context: the matrix that the uranium is found in can constrain the sources. For example, (Utsonomiya et al., 2004) found uranium in particles from coal combustion. Other measurements of particles known to contain uranium have been made in the laboratory using thermal ionization (Stoffels and Lagergren, 1981; Kraiem et al., 2011), laser-induced breakdown spectroscopy (Fichet et al., 1999), laser ablation (Gieray et al., 1998), and secondary ion mass spectrometry (Ranebo et al., 2009).

In contrast, the particles described here were sampled by a mass spectrometer that flies on a research airplane to measure the composition of particles with no sample preparation. No special attempt was made to sample radiogenic or fissile material during atmospheric measurement campaigns performed with the spectrometer. Of particular interest is a particle apparently containing enriched uranium that was sampled by chance during one campaign at an altitude of about 7 km near the Aleutian Islands.

The Particle Analysis by Laser Mass Spectrometry (PALMS)

instrument samples the composition of single particles in the atmosphere with diameters between about 200 nm and 5 μm. Particles are brought into a vacuum and, when detected, hit with a pulse from a 193-nm laser as they travel through the instrument (Fig. S1). A time-of-flight mass spectrometer collects the entire mass spectrum of ions produced by the laser ablation. The mass spectrometer can record single spectra with high dynamic range, which aids in seeing isotopes of even minor species in the particles. PALMS also measures the diameter of each sampled particle, specifically the vacuum aerodynamic diameter which for spheres is the product of the geometric diameter and the density relative to $1.0\,g\,cm^{-3}$. The density enters to the first power rather than the square root often associated with aerodynamic diameters because the particle was smaller than the mean free path of air at the pressure in the portion of the PALMS vacuum inlet where the particle velocity is determined.

The PALMS instrument was originally constructed for high-altitude sampling (Thomson et al., 2000; Murphy et al., 2014) and has since been improved and converted for other research aircraft. Over the course of about 20 years PALMS has measured the composition of millions of particles in a wide variety of environments from 200 m above polar ice to 19 km in the tropical stratosphere. In August 2016 PALMS was sampling on the NASA DC-8 aircraft as part of the Atmospheric Tomography (ATom) program (https://espo.nasa.gov/missions/atom/content/ATom). The purpose of the field campaign was to obtain some of the first global cross-sections of the concentration of trace gases and of dust, smoke, and other particles in the remote troposphere over the Pacific and Atlantic Oceans.

1.1. Data

The particle under discussion was sampled on a research flight from Anchorage, Alaska to Kona, Hawaii at an altitude of about 7000 m above the Aleutian Islands on 3 August 2016 at 20:40 UTC. Fig. 1 presents the mass spectrum of the particle. Laser ablation of particles produces ions that are mostly either elements or fragments of the original molecules and rarely, parent peaks for the molecules. From the peak areas in the figure, the uranium ions are over 2% of the total ions produced by the laser ablation of this particle, one of the largest U signals seen in the history of the instrument. Most significantly, ^{235}U is $3.1\pm0.5\%$ of ^{238}U. This corresponds to low-enriched uranium typically used in nuclear reactors, whereas natural uranium contains only about 0.7% ^{235}U and weapons-grade uranium is enriched up to around 90% ^{235}U or more.

One must be confident that the m/z 235 peak is from ^{235}U. The strongest evidence is that, within uncertainty in the peak areas, the isotope ratio is the same for the doubly charged ions at m/z 117.5 and 119 as for m/z 235 and 238. This shows that m/z 235 is not due to a molecular ion; in the PALMS instrument doubly charged peaks are generally observed only for atomic ions. Although implausible, one must consider the possibility that some unusual spatial or energy separation during the laser ablation produced a "shoulder" on the 238 peak that happened to be both separated from the main peak and occur at m/z 235 rather than any other place. There are several lines of evidence against this. First, in Fig. 1 no other ion has such a shoulder. Second, three mass units would be a very large separation in a mass spectrometer that is compensated for initial ion energy and position. For example, one could hypothesize that the m/z 235 peak is due to ^{238}U ions that originated from a fragment of the particle that ended up in a different spatial position in the ion source than the main peak. But creating ions that arrive at the detector three mass units before their nominal arrival time would require a spatial separation that is not only many times larger than the diameter of the particle but also outside the ionization laser beam. Finally, the ratio of m/z 117.5 to 119 helps exclude the possibility that the m/z 235 peak is an artifact of the ionization mechanism. The production of doubly charged ions is very sensitive to ionization conditions, so any unusual ionization mechanism would be unlikely to produce the same amounts of singly and doubly charged ions. Singly and doubly charged uranium ions also have different loss rates as they interact with ablated neutral molecules (Gieray et al., 1998). Overall, we do not know of a plausible way to produce the observed spectrum unless the m/z 235 and m/z 117.5 peaks are from $^{235}U^+$ and $^{235}U^{++}$. The implausibility of creating an anomalous 235 peak in the ion source must be balanced against the rarity of ^{235}U.

The uncertainty in the isotope ratio is determined from the consistency of the singly and doubly charged ion ratios (about 0.2%) and the accuracy of PALMS for known isotopic ratios of similar size from other elements such as K or Fe (often about 10% of the smaller isotope). The UO^+ and UO_2^+ peaks show that the uranium was present as an oxide. The uranium peaks are broader than low-mass peaks in the spectrum such as C^+ and V^+. One reason is that uranium oxide is refractory. The ions formed from vaporized uranium oxide have more thermal energy, which broadens the peaks.

The largest peak in the mass spectrum is vanadium, and other major peaks include K^+, Fe^+, NO^+, and SO^+. The latter two peaks are most likely from nitrate and sulfate, which often condense on particles during atmospheric transport. There are a number of smaller peaks containing carbon. Vanadium in fine particles is considered a tracer for heavy oil combustion (Zoller et al., 1973; Viana et al., 2009). Except for the uranium, we have observed spectra similar to Fig. 1 in many particles, often at low altitude over the ocean near shipping lanes. Without
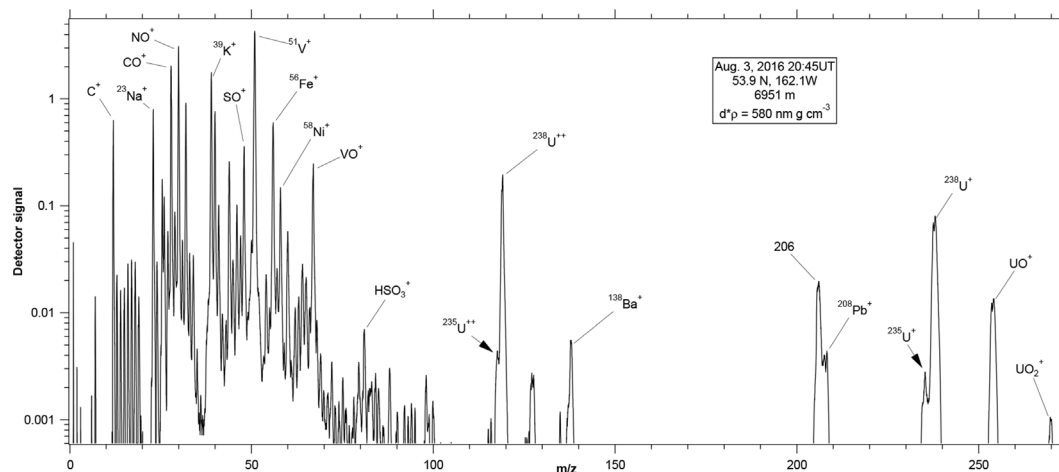

Fig. 1. Mass spectrum of the particle containing enriched uranium. The NO^+ peak indicates nitrates, SO^+ and HSO_3^+ sulfates, and abundant vanadium is usually a marker for heavy fuel oil. Many of the small, unmarked peaks at m/z < 100 are small fragments of organic molecules.