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U, Pu, and Am Nuclear Signatures of the Thule Hydrogen Bomb Debris

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This study concerns an arctic marine environment that was contaminated by actinide elements after a nuclear accident in 1968, the so-called Thule accident. In this study we have analyzed five isolated hot particles as well as sediment samples containing particles from the weapon material for the determination of the nuclear fingerprint of the accident. We report that the fissile material in the hydrogen weapons involved in the Thule accident was a mixture of highly enriched uranium and weapon-grade plutonium and that the main fissile material was ²³⁵U (about 4 times more than the mass of ²³⁹Pu). In the five hot particles examined, the measured uranium atomic ratio was $^{235}\text{U}/^{238}\text{U} = 1.02 \pm 0.16$ and the Pu-isotopic ratios were as follows: $^{240}\text{Pu}/^{239}\text{Pu} = 0.0551 \pm 0.0008$ (atom ratio), $^{238}\text{Pu}/^{239+240}\text{Pu} = 0.0161 \pm 0.0005$ (activity ratio), $^{241}\text{Pu}/^{239+240}\text{Pu} = 0.87 \pm 0.12$ (activity ratio), and $^{241}\text{Am}/^{239+240}\text{Pu} = 0.169 \pm 0.005$ (activity ratio) (reference date 2001–10–01). From the activity ratios of $^{241}\text{Pu}/^{241}\text{Am}$, we estimated the time of production of this weapon material to be from the late 1950s to the early 1960s. The results from reanalyzed bulk sediment samples showed the presence of more than one Pu source involved in the accident, confirming earlier studies. The $^{238}\text{Pu}/^{239+240}\text{Pu}$ activity ratio and the $^{240}\text{Pu}/^{239}\text{Pu}$ atomic ratio were divided into at least two Pu-isotopic ratio groups. For both Pu-isotopic ratios, one ratio group had identical ratios as the five hot particles described above and for the other groups the Pu isotopic ratios were lower ($^{238}\text{Pu}/^{239+240}\text{Pu}$ activity ratio ~ 0.01 and the $^{240}\text{Pu}/^{239}\text{Pu}$ atomic ratio ~ 0.03). On the studied particles we observed that the U/Pu ratio decreased as a function of the time these particles were present in the sediment. We hypothesize that the decrease in the ratio is due to a preferential leaching of U relative to Pu from the particle matrix.

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Introduction

In January 1968, a B52 airplane crashed on the sea ice about 12 km west of the Thule air base, NW Greenland. The aircraft was carrying four hydrogen nuclear weapons. The impact triggered the conventional explosives within the weapons and the explosion pulverized the fissile material in the bombs. The debris was scattered around the point of impact and some square kilometers of the ice was contaminated. The benthic marine environment received the fraction of the weapon material that was not recovered from the ice during the clean-up operation following the accident and probably also a fraction injected during the accident, as the impact caused part of the ice to break up (1–4).

Until now the source term and characteristics of the four disintegrated weapons have been poorly described in the open literature. The source term is an important aspect to know when dose assessments and environmental impact studies are to be conducted in a contaminated area. For the first 30 years, all studies were focusing on the increased levels of Pu and Am in the area as well as the transfer of these elements into the Arctic food web. The fissile material in the weapons were assumed to be a plutonium device and no investigations concerning uranium can be found. Later, some investigations using ICP-MS and high-resolution α spectrometry for the determination of the $^{240}\text{Pu}/^{239}\text{Pu}$ isotopic ratio suggest that the debris consists of different Pu sources (5–8). However, since the ratios were determined on bulk sediment samples, the ratios could represent a mixed ratio of different sources and the uniqueness from each source could not be determined. To identify the characteristic nuclear fingerprints in such areas, one should study single isolated hot particles, which most probably are fragments of the weapon material and consist of nuclides from one single source.

It took 31 years before the first report of uranium in the Thule accident was published (9). This hot particle study showed that Pu and U coexisted in the weapon material. One explanation that U was not reported earlier may be that all analyses were conducted on bulk sediment from the area. It is very easy to study Pu originating from the accident in these sediments as the levels are much higher than the Pu fallout levels. For U it is the opposite; the additional contribution from the accident might have been some kilogram of high enriched uranium spread out on some square kilometers of the sea floor and one can estimate that in the top 10 cm of the sediment in such an area there exist about 100 kg of natural uranium, so the accident U isotopic signature would to a great extent be blurred out with the isotopic signature of natural U.

Studies on isolated particles from the Thule sediment have shown higher $^{235}\text{U}/^{238}\text{U}$ ratios than the natural U isotopic composition (10, 11). In a recent study using secondary ion mass spectrometry (SIMS) to study single hot particles (10), it was shown that the Thule particles consist of different weapon-grade Pu and highly enriched U isotopic compositions; however, no U/Pu ratios were reported. One of the challenges of working with hot particles are the determination of the U isotopic composition, as these particles typically contain a tenth of a nanogram of uranium, and these amounts are typically procedure blank values of U conducted in normal laboratories, so the radiochemistry must be conducted under ultrapure conditions, preferably in clean laboratories.

In the present study the complete isotopic signature and the age of the nuclear material involved in the Thule accident are determined. It focuses on the actinides, U, Pu, and Am

in five isolated particles that have been totally dissolved under ultraclean conditions to ensure no bias of the $^{235}\text{U}/^{238}\text{U}$ ratio. In addition, retrospective analyses of bulk samples, where the activity most probably originated from one single particle, completed the determination of the Pu isotopic ratios ($^{240}\text{Pu}/^{239}\text{Pu}$ and $^{238}\text{Pu}/^{239+240}\text{Pu}$).

Experimental Section

The particles were separated from the top sediment (0–9 cm). The sediments were sampled by sediment corers close to the point of impact of the Thule accident, during the sampling expeditions to Thule in 1979, 1984, and 1997 (4, 6). The particle separation technique has been described in detail elsewhere (12). Briefly, the technique is based on sample splitting, using the gamma emitting (59.54 keV, $n_\gamma = 35.9\%$) ^{241}Pu daughter ^{241}Am , as an indicator of hot particles. The splitting of the samples continued until only a few grains remained, including the hot particle. The hot particles were further identified and localized using real-time digital imaging systems.

Dissolution of (U,Pu) O_2 hot particles is notoriously difficult using mineral acids (13). We checked that complete dissolution of the particles had occurred by comparing the gamma activity, measured by a high-purity germanium (HPGe) detector on the whole particle, with the α activity of ^{241}Am determined after dissolution and chemical separation.

Different analytical methods were used to determine the elemental composition, activity, and mass of U, Pu, and Am in each particle. High-resolution inductively coupled plasma mass spectrometry (HR-ICP-MS) and alpha spectroscopy were used to determine the isotopic and element ratios and the masses and activities in the particles. The instruments used were a Micromass PlasmaTrace2 high-resolution ICP-MS with an x-flow nebulizer and passivated implanted planar silicon (PIPS) α detectors.

The particles were dissolved in a mixture of hydrofluoric acid and nitric acid (ratio 1:3) in high-pressure Teflon cells. The dissolution procedure began with 0.1 mL of HF and 0.3 mL of HNO_3 , which was evaporated to dryness, and this was repeated 30 times. Finally, 1 mL of HF and 3 mL of HNO_3 were added to the closed Teflon cells, which were then placed on a hot plate so that the mixture was under pressure for 24 h. The solution was then evaporated to dryness. In addition, one particle (later referred to as TPE) was dissolved in a microwave oven, CEM MARS 5. A mixture of 7 mL of HF, 7 mL of HNO_3 , and 1.5 mL of HCl was added to the Teflon cell and heated for 20 min in the microwave oven at a maximum pressure of 250 psi (17.2 bar) and a maximum temperature of 200 °C. Twenty-five milliliters of saturated boric acid was then added and the mixture was heated for another 20 min in the microwave oven, to break the Pu–fluoride complexes formed in the dissolution process. The solutions from both dissolution methods were evaporated to dryness and 3 times 0.3 mL of HNO_3 was added and evaporated to dryness, to ensure that all the fluoride complexes were destroyed. The dissolved particles were thereafter diluted in 50 mL of 5% HNO_3 (Ultra Pure Sea Star quality and $> 18 \text{ M}\Omega\text{-cm H}_2\text{O}$). The analysis of Pu and U was done on radiochemically separated aliquots of the sample solution as well as on radiochemically unseparated aliquots. The sizes of the aliquots were 0.2–1.5 mL, depending on the activity of the particle. Radiochemical separation was performed using ion exchange (AG 1 \times 4, 100–200 mesh, BIO RAD). To minimize the use of acid, 1.5 mL columns with 0.7 mL resin were used. All acid used was of Ultra Pure Sea Star quality, except HF which was of pro analysis Merck quality. Unused Savillex Teflon capsules were acid-washed in boiling 12 M HCl before use. The samples were prepared in a clean laboratory. These precautions were taken to reduce cross-contamination by naturally occurring uranium isotopes.

Subsamples of each dissolved particle solution were analyzed with chemical yield determinants as well as without. The chemical yield determinants are added to monitor the loss of a certain element in the chemical separation procedures and to determine the mass and activity of each radionuclide in the sample. As chemical yield determinants we used ^{233}U , ^{242}Pu , and ^{243}Am . The subsamples analyzed without chemical yield determinants were used to determine the isotopic ratios; this as well as all isotopic chemical yield determinants has impurities of the isotopes of interest in the sample and thereby could bias the isotopic ratio determination. In addition, procedure and machine blank samples were prepared to assess the background levels.

U, Pu, and Am Separation. The subsamples were evaporated to dryness and thereafter dissolved in 8 M HNO_3 . Pu(IV) was absorbed onto the columns. The eluate was collected for Am and U, which was then separated using the method described by Holm (14). Thorium was hereafter eluted with 9 M HCl, followed by the elution of Pu with $\text{NH}_4\text{I} + 9 \text{ M HCl}$. The samples were then evaporated to dryness and the samples intended for ICP-MS analysis were diluted to 3% HNO_3 solutions (10 mL). The samples measured by α particle spectrometry were electrodeposited onto stainless steel discs in accordance with the method described by Hallstadius (15).

^{241}Pu Determination. The ^{241}Pu was determined by the ^{241}Am ingrowths on Pu α discs. The Pu discs were remeasured 6 years after the first measurement (i.e., at the same time as when Pu was radiochemically separated from Am). As the ^{241}Am α spectra overlaps with the ^{238}Pu α energies, the calculated decay corrected counts from ^{238}Pu were subtracted from the total α counts in these channels.

Results

Particle Destruction. It is known that a (U,Pu) O_2 matrix is difficult to dissolve using mineral acids. Experiments performed at Risoe National Laboratory (1) have shown that 8–40% of the Pu remains undissolved in bulk Thule sediment samples when using the Aqua Regia leaching technique described by Talvitie (16). Incomplete dissolution of Thule hot particles have been reported in other studies, confirming this (11, 17). An alternative method for particle dissolution could be the use of fusion agents as KF and borate fusion approach (18, 19). However, the reported ^{238}U procedural blank values from this dissolution technique are similar to the amount expected in the particles (range from 50 to 100 ng (19)), and for that reason these procedures are not optimized for single hot particles studied for the U isotopic signature. To check if the particles in the present study were dissolved, the γ -ray measurements of ^{241}Am on the undissolved particle and the determined α activity (determined from an aliquot of the dissolved particle solution) were compared. A good agreement between the ^{241}Am activities in the particles determined by γ and α spectrometry were achieved (coefficient of determination, $R^2 = 0.9991$), indicating that the particles were totally dissolved using the methods described in this article.

Plutonium Content. The results from HR-ICP-MS can be seen in Table 1 and from α spectrometry in Table 2. The results from a UKAEA Pu reference material solution (sample number: UK Pu 5/92138) were in good agreement with the reported values in the certificate (the atomic ratios agreed within 0.01%). The mean atom ratio, $^{240}\text{Pu}/^{239}\text{Pu}$, for the five particles is 0.0551 ± 0.0008 (1 SD, $n = 5$) and the corresponding activity ratio is 0.2057 ± 0.0011 (1 SD, $n = 5$).

There is also good agreement between the two different analytical techniques, i.e., the HR-ICP-MS and α spectrometry for the $^{239+240}\text{Pu}$ measurements. The mean activity ratio of $^{238}\text{Pu}/^{239+240}\text{Pu}$ is 0.0161 ± 0.0005 (1 SD, $n = 5$) and $^{241}\text{Pu}/^{239+240}\text{Pu} = 0.87 \pm 0.12$ (1 SD, $n = 5$), and the mean activity

TABLE 1. Pu Isotope Content and Ratios in the Particles on Mass and Activity Basis As Measured by HR-ICP-MS

| particle id | ²³⁹⁺²⁴⁰ Pu (ng) | ²³⁹ Pu (ng) | ²⁴⁰ Pu (ng) | ²⁴⁰ Pu/ ²³⁹ Pu atom ratio |
|-------------|----------------------------|------------------------|------------------------|---|
| TPA | 2.51 ± 0.09 | 2.380 ± 0.088 | 0.133 ± 0.006 | 0.0544 ± 0.0017 |
| TPB | 4.37 ± 0.16 | 4.14 ± 0.15 | 0.232 ± 0.009 | 0.0558 ± 0.0013 |
| TPC | 10.66 ± 0.39 | 10.10 ± 0.37 | 0.559 ± 0.022 | 0.0559 ± 0.0011 |
| TPD | 28.9 ± 1.1 | 27.4 ± 1.0 | 1.521 ± 0.060 | 0.0554 ± 0.0012 |
| TPE | 32.2 ± 1.2 | 30.5 ± 1.1 | 1.709 ± 0.067 | 0.0541 ± 0.0011 |

| particle id | ²³⁹⁺²⁴⁰ Pu (Bq) | ²³⁹ Pu (Bq) | ²⁴⁰ Pu (Bq) | ²⁴⁰ Pu/ ²³⁹ Pu activity ratio |
|-------------|----------------------------|------------------------|------------------------|---|
| TPA | 6.52 ± 0.25 | 5.41 ± 0.20 | 1.111 ± 0.046 | 0.2056 ± 0.0065 |
| TPB | 11.35 ± 0.43 | 9.41 ± 0.35 | 1.943 ± 0.077 | 0.2065 ± 0.0049 |
| TPC | 27.6 ± 1.0 | 22.95 ± 0.84 | 4.69 ± 0.18 | 0.2042 ± 0.0041 |
| TPD | 74.9 ± 2.8 | 62.2 ± 2.3 | 12.75 ± 0.50 | 0.2050 ± 0.0044 |
| TPE | 83.5 ± 3.1 | 69.2 ± 2.5 | 14.32 ± 0.56 | 0.2071 ± 0.0041 |

TABLE 2. Pu Isotope Content and Ratios in the Particles on Activity Basis As Measured by α-Spectrometry (Reference Date: 2001–10–01)

| particle id | ²³⁹⁺²⁴⁰ Pu (Bq) | ²³⁸ Pu/ ²³⁹⁺²⁴⁰ Pu activity ratio | ²⁴¹ Pu/ ²³⁹⁺²⁴⁰ Pu activity ratio | ²⁴¹ Am/ ²³⁹⁺²⁴⁰ Pu activity ratio | age (years); determined by ingrowths |
|-------------|----------------------------|---|---|---|--------------------------------------|
| TPA | 6.22 ± 0.23 | 0.0167 ± 0.0010 | 0.75 ± 0.15 | 0.173 ± 0.010 | 43.8 ± 5 |
| TPB | 9.78 ± 0.35 | 0.0165 ± 0.0009 | 0.84 ± 0.13 | 0.172 ± 0.009 | 41.6 ± 3 |
| TPC | 26.38 ± 0.94 | 0.0158 ± 0.0008 | 1.06 ± 0.12 | 0.162 ± 0.008 | 36.3 ± 4 |
| TPD | 74.6 ± 2.8 | 0.0156 ± 0.0008 | 0.83 ± 0.11 | 0.172 ± 0.009 | 41.8 ± 2.4 |
| TPE | 84.1 ± 3.0 | 0.0158 ± 0.0007 | 0.86 ± 0.13 | 0.166 ± 0.009 | 40.4 ± 3 |

TABLE 3. Uranium in the Particles Measured by HR-ICP-MS

| particle id | ²³⁵ U (ng) | ²³⁸ U (ng) | ²³⁵ U/ ²³⁸ U atom ratio | ²³⁵ U/ ²³⁹ Pu mass ratio | sampling date |
|-------------|-----------------------|-----------------------|---|--|---------------|
| TPA | 9.28 ± 0.63 | 8.34 ± 0.57 | 1.112 ± 0.005 | 3.90 ± 0.30 | 1979–8–23 |
| TPB | 10.00 ± 0.68 | 12.02 ± 0.82 | 0.832 ± 0.003 | 2.41 ± 0.19 | 1984–8–11 |
| TPC | 13.98 ± 0.95 | 16.29 ± 1.11 | 0.858 ± 0.004 | 1.38 ± 0.11 | 1984–8–11 |
| TPD | 74.65 ± 5.06 | 65.34 ± 4.44 | 1.143 ± 0.004 | 2.73 ± 0.21 | 1979–8–23 |
| TPE | 34.75 ± 2.36 | 30.27 ± 2.07 | 1.148 ± 0.006 | 1.14 ± 0.09 | 1997–8–25 |

ratio ²⁴¹Am/²³⁹⁺²⁴⁰Pu is 0.169 ± 0.005 (1 SD, *n* = 5) in the 5 particles, reference date: 2001–10–01.

Uranium Content. The uranium results from the HR-ICP-MS measurements are shown in Table 3. These results show similar isotopic ratios for the five particles, ²³⁵U/²³⁸U = 1.02 ± 0.16 (1 SD, *n* = 5) which is equivalent to about 50% mass enrichment of ²³⁵U. The slightly lower ratio can be an effect of some cross-contamination of natural uranium, which has a much lower ratio. However, these samples were radiochemically separated and prepared in a clean laboratory and for the sub samples where the ²³⁵U/²³⁸U ratio was determined no radiochemical yield determinant (²³³U) was used, to minimize cross-contamination of uranium.

The mass ratio of the fissile material in the particles, ²³⁵U/²³⁹Pu, is less affected by natural uranium cross-contamination than the ²³⁵⁺²³⁸U/²³⁹⁺²⁴⁰Pu ratio (Table 3). It appears that the ratio decreases with the time the particle has been exposed to the marine sediment (Figure 1). We believe that the result reflects preferential leaching of the uranium from the particles.

Discussions

The published investigations concerning the Thule accident have historically been focused on plutonium and very little on uranium in the contaminated area. The Pu inventories and Pu and Am transfer in the food web have been the main interest in these studies (2–4). The source term was determined on bulk samples with α spectrometry and character-

ized with the isotopic signature of ²³⁸Pu/²³⁹⁺²⁴⁰Pu ratio and ²⁴¹Am/²³⁹⁺²⁴⁰Pu ratio.

It took several years before the first ²⁴⁰Pu/²³⁹Pu ratios were published (5–8, 20, 21). No unique values have been found in these studies as the ²⁴⁰Pu/²³⁹Pu isotopic ratios have been scattered (ranging from 0.022 to 0.059 atom ratio), which suggests that there is more than one unique source term of the Thule accident debris. These ratios were determined on bulk sediments and could be mixed ratios from different sources and the fingerprint from each source is then difficult to determine. Dahlgaard et al. (6) measured the ²⁴⁰Pu/²³⁹Pu atom ratios by HR-ICP-MS on 32 bulk sediment samples collected on the 1997 sampling expedition to Thule and plotted the ratio versus the activity in the analyzed sample. It is clear from Figure 2 (redrawn from Dahlgaard et al. (6)) that the high-activity samples are split into two groups, with mass ratios of 0.057 and 0.035. The mean ratio of these measurements is 0.0442 ± 0.0073. There is an indication of a group around the mass ratio of 0.043. However, these are samples from locations close to the point of impact, less than 1 km, and they are considered as low active for these locations, and possibly, they could be a mixture of the other sources and reflect the mean ratio between the sources rather than a group itself. However, that it should be a ratio group, rather than a mean ratio, is supported by the same Pu isotopic ratio found in one hot particle analyzed by Ranebo et al. (10).

To study the nuclear signatures of the sources present, single hot particles should be analyzed, which most probably

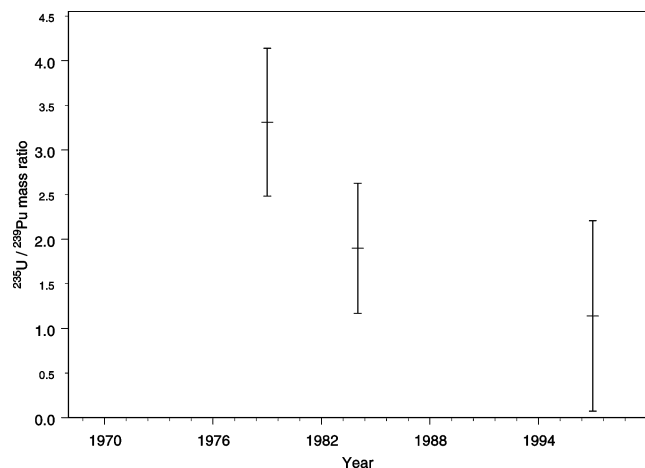


FIGURE 1. Mean mass ratio, $^{235}\text{U}/^{238}\text{Pu}$, in particles collected during a specific year. There is a tendency that the uranium content is lower in the particles exposed in the marine sediment environment for a longer time, which would mean that there is preferential leaching of uranium from the particle in the sediment. The standard deviation for the ratio in 1997 is the square root of the ratio, as only one particle has been analyzed from this year; the standard deviation from the HR-ICP-MS measurement is much less than that shown (see Table 3).

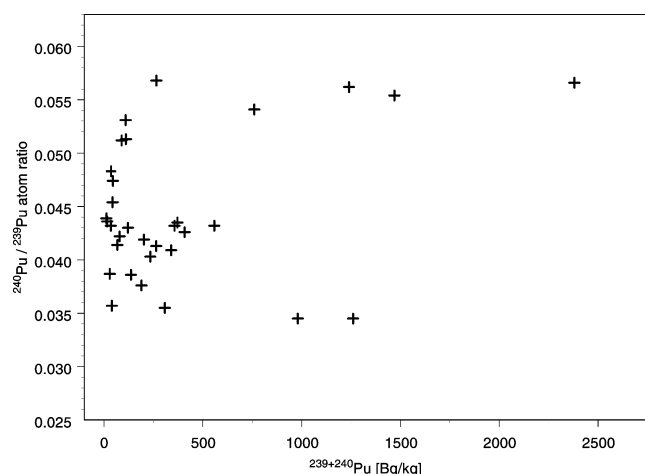


FIGURE 2. Graph showing the $^{240}\text{Pu}/^{239}\text{Pu}$ atom ratio in bulk sediment samples sampled in 1997. The atom ratios are grouped into two groups around 0.056 and 0.035 and a possible group around 0.043. Data from Dahlgaard et al. (6).

are fragments of the weapon components, i.e., originating from one single source. The results from the particles studied herein indicate only one single source with the isotopic ratios: $^{238}\text{Pu}/^{239+240}\text{Pu}$ activity ratio of 0.0161 ± 0.0005 , $n = 5$, and the $^{240}\text{Pu}/^{239}\text{Pu}$ atom ratio of 0.0551 ± 0.0008 , $n = 5$. The $^{240}\text{Pu}/^{239}\text{Pu}$ ratios are equal to the ratios observed by Dahlgaard et al. (6), Stürup et al. (7), and Mitchell et al. (8) in their most active bulk sample. Lind et al. (11) analyzed three Thule hot particles, all with equal $^{240}\text{Pu}/^{239}\text{Pu}$ atom ratios as the particles investigated in this study. Ranebo et al. (10) studied eight Thule hot particles by SIMS and found four different $^{240}\text{Pu}/^{239}\text{Pu}$ atom ratios. Five of these had a $^{240}\text{Pu}/^{239}\text{Pu}$ atom ratio similar to those of the particles in this study (around 0.058) and the other three particles had the ratios 0.042, 0.036, and 0.028, respectively. Concluding the $^{240}\text{Pu}/^{239}\text{Pu}$ isotopic atom ratio discussion, four characteristic groups have been identified from hot particle studies with the ratios of 0.028, 0.036, 0.042, and 0.056. And it also appears that most of the Thule debris originates from the source with a $^{240}\text{Pu}/^{239}\text{Pu}$ isotopic atom ratio of 0.056 and an $^{238}\text{Pu}/^{239+240}\text{Pu}$ activity ratio of 0.016. This, as all the five studied hot particles in this study and most of the hot particles studied by others (10, 11), has this ratio and a few other particles with lower ratios have been analyzed. One explanation, excluding the statistical possibility that the present study only has sampled particles from the "high Pu isotopic ratio group", could be

that this source, during disintegration, produced larger particles. This is also indicated from the bulk sediment samples, where the samples with the highest activity originate from this source. In addition, larger particles are more easily identified and separated than the small sized particles using the sampling splitting method. It cannot be determined whether the different sources originate from different weapons or from different parts within the weapons.

The activity ratio of $^{238}\text{Pu}/^{239+240}\text{Pu}$ in Thule sediments has been determined in several hundreds of samples over the past 39 years (2–4, 6, 22, 23). These ratios have been measured by α spectrometry performed on bulk sediment samples (0.5–5 g). The mean $^{238}\text{Pu}/^{239+240}\text{Pu}$ ratio from the sediments collected during the Thule 1984, 1991, and 1997 expeditions is 0.014 ± 0.004 ($n = 328$), decay corrected to 2001. This mean ratio is derived from the sediments close to the point of impact (within a radius of 8 km). In this area, the contribution of global fallout Pu (with an activity $^{238}\text{Pu}/^{239+240}\text{Pu}$ ratio of 0.025) is less than 1% of the Pu inventory. This mean ratio is lower than the ratios found in the five particles studied in the present paper, which support the theory that more than one unique source term should be present. However, since the plutonium activity in the sediment is, to a great extent, associated with hot particles (1), and high-activity samples have been analyzed, it could be possible to investigate the unique ratios of the sources

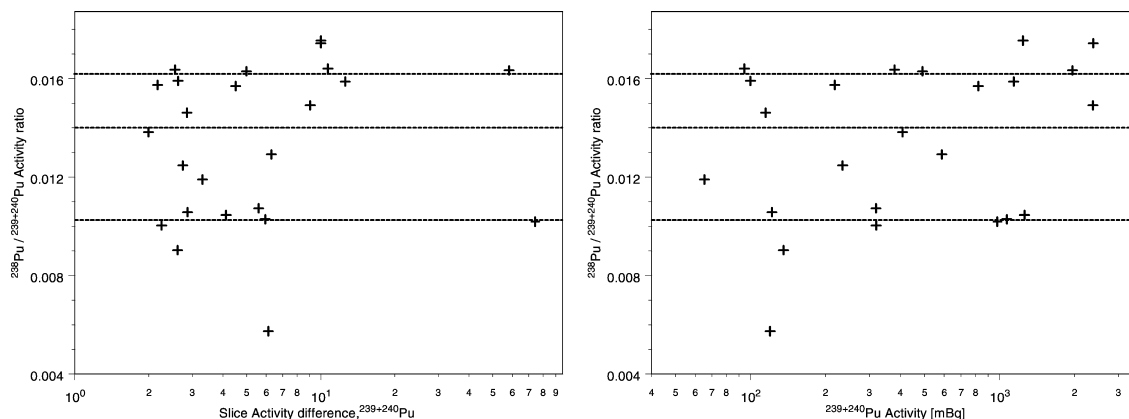


FIGURE 3. Two plots showing the $^{238}\text{Pu}/^{239+240}\text{Pu}$ activity ratios in bulk sediment samples. To the left are the ratios plotted versus the deviation from the mean activity of the activity concentration above and under the slice and to the right are the ratios plotted versus the activity concentration in the subsample. The ratios are grouped into two groups around 0.016 and 0.010, and there are very few observations close to the mean ratio of 0.014.

present in the sediment by applying some criteria to old data. One such criterion is to use the $^{238}\text{Pu}/^{239+240}\text{Pu}$ ratios in the subsamples with the highest activities, which are likely to originate from one single hot particle. The counting statistics in the α spectra of these samples are also better and so the uncertainty in the ^{238}Pu measurements from interfering peaks originating from the short-lived daughters from the thorium series is lessened. However, as the sediments at the point of impact have very high activity concentrations and numerous particles are present, a second criterion must be applied. Thus, the activity deviation between a particular sediment slice and the mean activity between the slice over and under this slice must be large; i.e., an abnormal activity concentration should be observed in the Pu sediment depth profile. We have performed such a study on the samples collected at the 1997 sampling expedition to Thule, fulfilling these two criteria. It is clear from Figure 3 that almost none of these samples have the calculated mean $^{238}\text{Pu}/^{239+240}\text{Pu}$ ratio of 0.014. The $^{238}\text{Pu}/^{239+240}\text{Pu}$ ratios are grouped more or less around two ratios of 0.016 and 0.010. In the plot to the left in Figure 3, the ratios are plotted versus the activity concentration deviation, i.e., the second criterion. The two samples with the largest deviation most probably originate from one single source (hot particle) and they have activity ratios of 0.0102 and 0.0163, respectively. In the right-hand plot of Figure 3 the ratios are plotted versus the activity concentration and it is clear that the samples with highest activity concentrations stretch out around the 0.016 ratio group. Assuming that only these two unique $^{238}\text{Pu}/^{239+240}\text{Pu}$ ratios are present and the mean ratio observed is 0.014, this would mean that two-thirds of the debris originates from the source with the $^{238}\text{Pu}/^{239+240}\text{Pu}$ activity ratio of 0.016. The high $^{238}\text{Pu}/^{239+240}\text{Pu}$ ratio is in good agreement with the five hot particles studied in the present paper. These particles all have higher activity (6–84 Bq $^{239+240}\text{Pu}$) than the analyzed bulk sediment samples, where the highest activities of the samples were about 2.5 Bq $^{239+240}\text{Pu}$.

The ^{241}Pu activity of the particles was calculated by ^{241}Am ingrowths on Pu α disks. The $^{241}\text{Pu}/^{239+240}\text{Pu}$ can be seen in Table 2. The mean activity ratio for the five particles was 0.87 ± 0.12 in October 2001. In Table 2 the calculated age (time since Pu was chemically separated from the Am) of the weapon-grade Pu material can be seen. The ages indicate that this fission material was produced in the late 1950s and early 1960s. This is in good agreement with Aarkrog et al. (4) who estimated the time of ^{241}Am extraction to be February 1960 ± 4 years. Moring et al. (17) estimated a younger age (1967 ± 3 years) of the material calculated in one hot particle.

$^{241}\text{Am}/^{239+240}\text{Pu}$ ratios have also been determined several times in Thule sediments (4, 6, 22–24). However, the ratios

have in some cases been determined on different aliquots, which often is the case in the analysis of high-activity samples. Therefore, the ratios determined are of no use in evaluating the unique source terms. The ratio is still increasing due to the decay of ^{241}Pu and will reach maximum ratio 73 years after the Am was radiochemically separated from Pu. To be able to compare ^{241}Am data sets from different Thule sampling expeditions, the amount of ^{241}Pu and the manufacture date of the different sources of the weapons must be known. It is probable that the ^{241}Pu content differs between the different sources in the Thule accident debris, as the $^{241}\text{Am}/^{239+240}\text{Pu}$ activity ratio reported shows large variations (5, 24). If the sources were made at different times, it would be very complicated to determine the expected current $^{241}\text{Am}/^{239+240}\text{Pu}$ activity ratios. The mean ratio of the five particles is 0.169 ± 0.005 (reference date: December 2001) and this ratio will reach its maximum around the year 2030 and then start to decrease to lower ratios.

Very few reports on uranium in the Thule debris have been published. In the investigated five particles in this study it is clear that the fissile material in the nuclear weapons involved in the Thule accident is a mixture of highly enriched U (about 50% mass enrichment of ^{235}U) and weapon-grade Pu. As only particles originating from one unique source have been analyzed for both U and Pu, this is at least true for these. It is most probably true also for the other Pu isotopic mixtures in the Thule debris, as no study has yet found a Thule particle consisting of only Pu without enriched uranium. Ranebo et al. (10) show that all the particles analyzed in the SIMS have high enriched uranium mixed with the Pu. The $^{235}\text{U}/^{238}\text{U}$ atom ratio ranged from 0.959 to 1.437 in their study. This is in good agreement with the ratios of the five particles ($^{235}\text{U}/^{238}\text{U} = 1.02 \pm 0.16$) we analyzed with the ICP-MS technique, also showing that only limited cross-contamination from natural U was introduced in our method.

As shown in Figure 1, the $^{235}\text{U}/^{239}\text{Pu}$ mass ratio is decreasing with time, indicating that uranium is leaving the particle lattice. With the belief that this represents a preferential leaching of uranium compared to plutonium, the estimated mass of ^{235}U was around 4 times the mass of ^{239}Pu in the fresh accidental debris. Preferential leaching has been demonstrated in several experiments conducted in laboratories where the leaching/corrosion of UO_2 from nuclear fuel has been studied (25, 26). In these experiments (conducted in alkaline as well as acid salt solutions of different types) most data indicate a stronger release of uranium than plutonium. These studies can partly explain the decreasing U/Pu ratio with time, shown in Figure 1. It can be seen in the figure that the $^{235}\text{U}/^{239}\text{Pu}$ ratios are associated with large

variations for a specific year. The large variance in the ratios can be explained by the fact that few particles are compared each year and also to some extent by the fact that the particles move up and down in the sediment as a consequence of the bioturbation combined with the leaching rate probably being a function of sediment depth, interstitial water chemistry, sediment coating, and particle composition. When considering particle dissolution and potential release of weapon plutonium and uranium, it has also to be considered that over time most of the particles will reach sediment depths where oxid dissolution kinetics may not be applied (e.g., the UO₂ model by De Pablo et al. (26)), as during oxygen-deficient or anoxic conditions uranium may not become oxidized and thus the particle dissolution rates may be significantly reduced. Röllin et al. (25) observed UO₂ dissolution rates that were a factor of 1000 less under reducing conditions than those in oxid conditions with the same bicarbonate concentrations for both cases. On the other hand, dissolution rates of plutonium were only reduced by a factor of 10 in the same experiment.

The particles formed during the Thule accident are however likely to be rather different compared to the spent UO₂ fuel. The specific surface area (porosity of particles) is probably different due to fast cooling after the fire at Thule. The particles formed at Thule may be treated as site-specific particles and be regarded as a unit of their own. Knowledge on their dissolution and corrosion rates may be derived only from experiments conducted with the very same material.

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