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Assessment of weathering and leaching rates of Thule hot particles

Per Roos (1)
Iisa Outola (2)
Ulrika Nygren (3)
Henrik Ramebäck (3)
Rajdeep Sidhu (4)

(1)Risoe National Laboratory for Sustainable Energy
Technical University of Denmark
(2)STUK-Radiation and Nuclear Safety Authority, Finland
(3)FOI CBRN Defence and Security, Sweden
(4)Environmental Monitoring Section, Health and Safety Department
Institute of Energy Technology, Norway

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Abstract

Within the current project a methodology for separating actinide particles originating from the Thule 1968 accident has been developed. Particles were completely isolated in water using visual and radiometric methods. The particles were attached electrostatic to a plastic support and could easily be moved to any container for leaching studies or other type of studies. Leaching and dissolution studies performed within the project indicate that some particles are relatively easily destroyed or leached while others are more refractory. The results shows that even though the oxide particles are hard to completely dissolve they release material even when exposed to weak solvents like water and salt solutions. Exposures to lung simulant fluids show relatively slow dissolution rates comparable to what is found using only water. Sequential extraction of particles shows that variation between particles is very large; some dissolve easily while some does not. Of radiological importance is the disruption of particles when exposed to dissolution.

Key words

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Final Report from the NKS-B HOTRATE activity (Contract: AFT/B(09)6)

Per Roos[1]
Iisa Outola[2]
Ulrika Nygren[3], Henrik Ramebäck[3]
Rajdeep Sidhu[4]

[1]Risoe National Laboratory for Sustainable Energy, Technical University of Denmark
[2]STUK-Radiation and Nuclear Safety Authority, Finland
[3]FOI CBRN Defence and Security, Sweden
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1. Introduction

During the cold war US strategic bomber aircrafts carrying nuclear weapons were constantly patrolling American air space and borders to the Soviet Union. This was part of the US Air Force Strategic Air Command (USAF SAC) developed after the World War II. The mission routes involved both daily transatlantic B-52 flights to Italy and Spain but also northerly flights to Greeland. The construction and use of the Thule Air Base in the patrolling missions became an important point in the US military strategy to better provide SAC with a offensive capability in the event of a Soviet first strike and provide a significant cold war nuclear deterrant. The construction of the Ballistic Missile Early Warning System (BMEWS) at Thule in 1959 reduced the number of northerly flights but also involved Thule Monitor Missions where nuclear armed B-52 aircrafts should act as a back-up communication link between the BMEWS and the North American Aerospace Defence Command. These flights were geographically specified to Baffin Bay and areas around Thule. On January 21, 1968, the B-52G Stratofortress bomber 'HOBO 28' took off for a 24h Thule Monitor Mission with 7 crew members. After some hours flight a series of problem with cabin heating eventually resulted in a cabin fire which forced the crew to abandon the aircraft before they could carry out an emergency landing at Thule Air Base. Six crew members ejected safely but one was killed while trying to bail out. The bomber cashed on the ice in North Star Bay about 12km west of Thule Air Base. The conventional high explosive component of the four 1.1 megaton B28FI (originally Mk28) hydrogen bombs ignited together with the aircraft fuel and caused dispersion of weapons plutonium, uranium, aericium and tritium. The impact and explosion did not trigger any fission. Dispersion of weapons material was mainly confined to a 150 x 850 m^2 blackened area stretching south from the impact point although contamination was recorded at an early stage also at more distant locations such as Saunders Island and the Narssarssuk area west and south of the impact point respectively. A clean-up operation "Project Crested Ice" was initiated to remove contaminated ice and snow and transport it back together with the aircraft wreckage and retrieved weapons components to the US. Since the accident around 10 expeditions have been conducted to the Bylot Sound area to investigate the extent of contamination on the seabed. During this time focus has entirely been on marine investigations due to the main pathway to the local Inuit community being consumption of marine foods. Concern about the potential contamination to the terrestrial sites has been very limited.

2. Source material for the project. Sample collection at Thule 2003-2008.

In 2003 a few samples of soil were collected on land about 10 km south of the impact point. The presence of relatively high concentrations of Pu in several of the collected samples prompted for further investigations of the site, which took place between 2006 and 2008. Reporting of findings in the 2003 expedition is presented in Nielsen and Roos (2006). During these expeditions some 500 soil samples were collected over an area approximately 30 km^2. In parallel portable NaI-detectors were used to monitor the presence of the ^{241}Am 59 keV line both placed on the ground (Figure 1 below) and held in air to cover a larger area and provide an average value. The detectors were used to localize larger particles but the majority of particles were isolated in the large amount of soil samples collected during the three sampling campaigns. It was early recognized that the occurrence of actinide particles on land from the accident at Thule is very patchy. In general activity is associated to hot spots ranging from less than a meter to several tens of metres. The particles used in the current project were all sampled from a hot spot discovered already in 2006 and which is located close to the

Narssarssuk houses. The size of this hot spot is approximately 50 x 50 m. Soil samples from this spot were taken using both spades and tubes (10 cm diameter) to depth of 3-15 cm depending on presence of stones.

Figure 1: Soil collection at Thule (left) and gamma screening of soil using a portable NaI-detector (right).

3. Isolation of Thule Actinide particles

The term 'hot particles' has been debated and is still being debated as being an appropriate description for the kind of particles being dealt with here. The alternative term 'environmental radioactive particles' or 'actinide particles' may be more appropriate depending on the situation. Due to the nature of the Thule particles we will throughout this report use the term 'actinide particles' when referring to them. In radiological sciences the term 'Hot particles' as such is an operational defined type of radioactive cluster of one type or another. For practical reasons they are defined from the instruments we use to detect them. There is no general definition that limits what a 'hot particle' is, nor what composition or size it has. The dose-rate, environmental behaviour as well as their behaviour in biological systems is more complex than can be covered by the models we normally use to assess exposure from environmental radioactivity. While our knowledge of environmental radioactivity from the natural occurring radioisotopes and from artificial radioisotopes introduced by military and peaceful nuclear activities is relatively solid our understanding of hot particle behaviour in general is not. Simply because the number of studies on such particles are very limited. Unfortunately, from present observations, understanding hot particle behaviour is a site-specific phenomenon where particle behaviour is depending on both the history of creation and the specific environment they have been exposed to. Even within these narrow borders variation between individual particles may be large. We should also bear in mind that the tools presently used to determine particle properties might be inappropriate for a relevant description of their behaviour. The interaction between these particles and their environment depends not only on surface properties and chemistry but also on mechanical stability, morphology, solid-state structure and the way particles are being transported around in their environment. The entire spectrum of biochemical reactions and how this affects the particles in the long run is obviously also a complex matter and is in general out of reach in the present scientific community. The variability of various properties for a given particle population, even when isolated from a single site, may thus be larger than what we can estimate from present knowledge. With respect to possible studies on available particles, some parameters are easy to study, some nearly impossible. Experimental 'recipes' for such studies on micrometer-sized objects does not exist and the methodology itself is therefore an important

part of any project on 'hot particles'. The present project aims at being a start of the study of properties specifically of the actinide particles dispersed during the Thule accident in 1968

A general trend in environmental science laboratories today is an increased stringency in how to handle chemicals, waste and radioactive isotopes. Permissions, accreditation and regulations of various kinds are becoming more and more accepted in the everyday work, unfortunately most often without parallel improvements in personnel competence on actual handling of hazardous products. One of the issues faced in this project was how to safely handle the radioactive particles of interest. While in many laboratories pipettes used to handle actinide tracer solution are treated as radioactive waste even if they only holds a few mBq the same laboratories should be able to handle and separate radioactive particles having hundreds of Bq or even kBq activities of Pu-isotopes. Several of these laboratories work on analysing actinides at 'normal' environmental levels meaning samples with activities in the mBq range. Several orders of magnitude lower than what is found in single typical Thule particles being studied in this project. An important part of the work with actinide or other hot particles is therefore methods of safe handling, which means ensuring both a minimum of exposure to persons working with them but also preventing contamination of laboratory space and equipment. Methods on how to deal with the actual handling of particles were therefore an important part of the project. This part of course had to be merged with the need to be able to obtain particles in a reasonably easy way with a minimum of disturbance of the particles themselves.

Isolation of individual 'environmental radioactive particles' is a fundamental step in order to be able to characterize and understand the nature of them. Analysis of bulk material can provide some information about general solubility but if detailed knowledge about morphology, appearance and dissolution behaviour is to be gained isolation of individual particles are necessary. The identification of Thule 'hot particles' was described already in the early reporting of the accident (Report Crested Ice; Figure 2) but little attention was paid to them. Eriksson et al (2002) isolated the first particles from seabed sediments using a sample splitting technique based on the ^{241}Am 59 keV gamma-line and in the end used a digital image system to localize the particle. Using this technique, the particles were not completely isolated from other grains of sand and soil. The existence of the particle was therefore not confirmed until placed in a SEM with EDX where L and M-lines from U and Pu could be observed. Backscattered electrons from high Z material could also be used to further confirm the presence of a actinide particle. The advantage of using this approach is that particles of nearly any size could be tracked as long as the emission of the 59 keV gamma-line could be detected during a reasonable counting time. For the Thule actinide particles with size of about 10 μm, count rates of the ^{241}Am 59 keV line in the order of 0.1 cps or less can be expected using an ordinary 10-20% HPGe-detector with a Be or C window. For particles of about 1 μm count rates in the order of 1 count per 1000 to 10 000 seconds are to be expected. Thus close to or less than the detection limit. For isolation of particles in this range, track-etch films or digital autoradiographic devices are more suitable. The time to isolate a particle with size in the order of 10 μm from a 50 g soil or sediment sample using the sample splitting techniques above is typically in the order of 1-2 hours. Then follows time for the identification of the particle using a digital image system and time for analysis in the SEM.

Figure 2. Early separation of 'hot particles' from melted ice and snow close to the impact point at Thule. Tracks created by the particle emissions visible by the autoradiographic technique (right).

The main drawback of the method is that the particle has to be fixed on to some adhesive conductive tape in order to be placed in the SEM. The positioning of the particles onto adhesive conductive tape is ideal as long as investigations are made using techniques where charged particles are used to bombard it (eg PIXE, SEM, SIMS etc). The placing of the particle onto adhesive tape however sets restrictions on what further investigations can be made (e.g. particle dissolution and leaching studies). During such conditions it may be necessary to move the particle between various containers (e.g. Teflon beakers, small columns or plates) with a minimum of disturbance from other material. It is possible to remove the particles from adhesive tape using solvents or by mechanical means but it may introduce unwanted solvents to the system or involve an extra risk in the form of loosing the particle to an unknown location. Also, due to the presence of several other sand and soil grains present on the tape isotopic analysis of uranium in particular will be biased towards more natural isotope patterns. Also the chance of finding minute amounts of trace elements present in the particles will be hampered by the bulk matrix following the particle.

Alternative ways of localising particles are using track-etch films or digital autoradiographic systems but the problem of completely isolating the particle free from surrounding grains is nearly impossible only using these techniques. Examples of tracks in ordinary CR-39 film exposed to a few milligrams of Thule soil is presented in figure 3. Since Thule actinide particles are made up of a mixture of both uranium and plutonium the sucessive leaching of these particles involves observing the behaviour of both elements. Uranium is present in most environmental materials and chemicals at concentrations that would alter the characteristic uranium isotope ratios of any given particle. The presence of other material than the particle itself is thus to be avoided if possible.
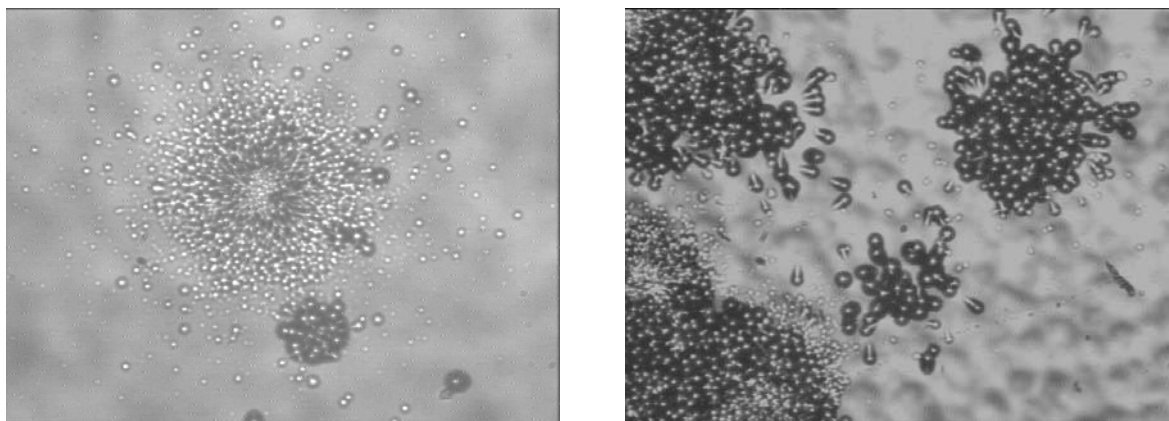
Figure 3. Low-power microscope pictures of CR-39 film exposed to a few milligrams of Thule soil. The size of individual tracks are about 10 μm.

At sizes of around 10 μm and above Thule actinide particles are visible using a low-power microscope or a loupe. During early work with the first terrestrial Thule samples (2003) it became evident that particles were normally present as single units, not incorporated into other material and with a characteristic black metal shiny appearance. These characteristics made it relatively easy to separate the actinide particles visually even from hundrends of other grains present in the field of view of a low-power microscope. The problem of handling such material safely then became of importance. The sample splitting procedure of dry samples creates dust which therefore should be performed during ventilated conditions and far away from labware being used for actinide analysis at environmental levels. When reducing the sample size to some hundred grains the ventilation however creates a problem by movment of light material, including the actinide particle and soil grains. The risk of loosing the particle to an unknown location risking inhalation, ingestion and/or contamination of the laboratory is obvious. By instead immersing the soil particles in water at an early stage the handling becomes more safe in several aspects. Using pipettes to move the soil grains and in the end a low-volume (μL) pipette the actinide particles can be handled individually. By placing the final ~50 soil grains on a hydrophobic surface (eg a plastic surface) with water the water drop will act as a lens which further provides optical benefits (Figure 4). Using the pipette the particle can safely be moved to any surface for further investigation. Letting the particle sink to the surface makes it normally also possible to pipette away the water used to transport the particle thus further removing potential contamniating material (specific problem when analysing for uranium isotopes). The use of water to handle the soil and particles also permits work to be done almost everywhere and is not bound to be done in a fume cupboard. Since the work in practice requires a great deal of focus and attention comfortable working conditions greatly improves safety and quality of the work.

Figure 4. Two isolated Thule actinide particles placed in a drop of water. Photographed using an ordinary loupe and a camera with macro settings. The particles were about 50 μm and had an activity of 55 and 40 Bq ^{241}Am respectively.

Even though SEM-pictures of the Thule actinide particles are among the most valuable type of information (for morphology) obtainable the larger particles can also be pictured using ordinary visual microscopy. As mentioned above SEM requires the particle to be placed on a conductive adhesive tape. Such tapes are usually not transparent and therfore limits possibilities of using visual microscopy. Examples of visual microscopy pictures are seen in Figure 5.


Figure 5. Optical microscopy pictures of two larger Thule actinide particles (fragments). Size of particles can be determined from the 50 μm bar in the pictures.

4. Characterization of Thule actinide particles within 'HOTRATE'

The characterization of particles performed within the current project was leaching of the Thule actinide particles using weak solutions (water and salty solutions), lung- and stomach simulant fluids as well as using a sequential extraction procedure. One of the particles was also determined with respect to isotopic and elemental composition.

4.1 Leaching with weak solvents

Within the NKS HOTRATE project a pilot study on particle characterization with respect to leaching techniques and determination of particle composition was undertaken. Techniques for dissolution of particles and determination of the elemental and isotopic content was performed as well as micro-techniques for performing sequential extraction using reagents of various kind. Among these reagents were standard sequential extraction and body fluid simulants such as stomach fluid simulant and lung fluid simulant. It was early recognized that the leaching behaviour of the Thule actinide particles is very complicated. Especially when leached with weak solvents the surface properties are crucial. Methods devoted to morphology and surface properties of the particles should be further developed. Parallell to these studies surface studies using photoelectron spectroscopy (XPS) and time-of-flight SIMS (TOF-SIMS) have been elaborated upon to evaluate properties of the very outer surface (a few Å). This work is ongoing. An example of the complicated behaviour when leaching with only water (18 MΩ) is seen in Figure 6. The particle was placed in a small 1 ml column with a 0.2 μm filter and leached sucessive times with 0.5-2 ml water during 1-20 minutes. The leaching period for this particle ranged over a period of 2 months and time between leaching events varied between 1 hour and 7 days. The water used for the individual leaching events were acidified with HNO_3 and analysed by ICP-MS without any further treatment specifically for U & Pu isotopes. The results for one of the particles are shown in Figures 6 to 8. After the 13 leaching event a single leach using 0.5ml of 0.1M $MgCl_2$ during 10 minutes was applied.
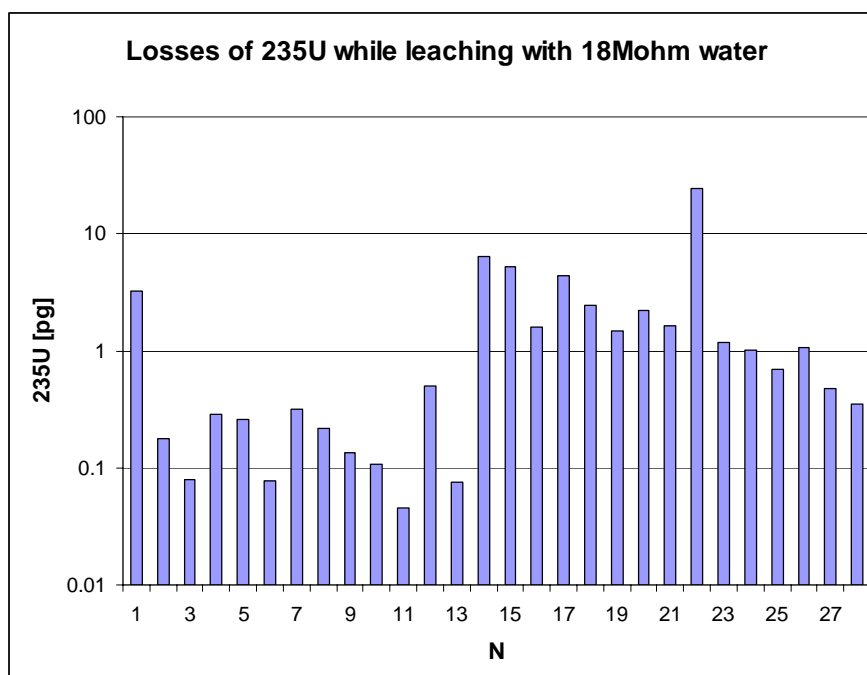

Figure 6. Losses of [235]U from one of the Thule particles when leaching with pure water. Leaching No 13 was done using 0.5 ml of 0.1M $MgCl_2$ during 10 minutes. After this event leaching continued with water only.

Clearly, losses of ^{235}U increased significantly after the particle was exposed to the weak MgCl$_2$. This indicates a change of surface properties due to the exposure of the weak conductive salt solution. Possibly a coating present on the particle became partially removed during this treatment. The presence of very thin coatings on the surface of the particles have been observed using TOF-SIMS where only the very outer surface layer is exposed. Figure 7 shows a TOF-SIMS spectrum of U and Pu isotopes obtained from another particle being studied. Clearly, surface coating of the particle is present. The TOF-SIMS ionisation is effective only at some few nm range so coatings are in that order of magnitude. The particle appearance after 8 hours sputtering is seen in Figure 8. Even though the support plastic adhesive film has been heavily eroded (melted) the particle itself has only been gently scratched on the surface using the technique. From the magnitude of the various elements detected with the TOF-SIMS the surface coating seems to be made up of ordinary organic coating containing carbon, nitrogen and oxygen and naturally water. However, any handling of these particles will introduce a surface coating by water and simple carbon compounds present in air. In any case, first when sputtering away this surface coating the U and Pu signals appear. The coating of the surface is an important parameter since it protects the erosion and leaching of the particle. Considering the actinide particles as metal oxide particles it would not be surprisongly to see coatings of iron, manganese and several other oxide-forming metals on the surface. For the particles studied so far coating by organic material and silica (probably colloidal silica particles) has been the dominating material.
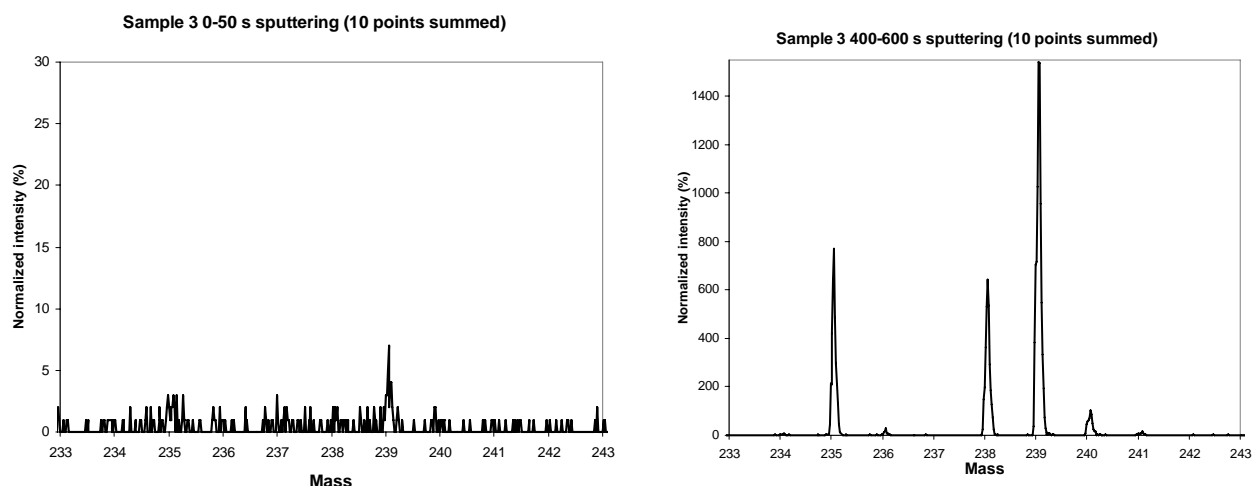

Figure 7. TOF-SIMS spectra of U & Pu signals obtained from the surface of a Thule particle with initial sputtering (left) and after some 500s of sputtering. The sputtering depth using the settings applied in this case is in the order of some tens of nanometer per 100s. The relative sensitivities of Pu and U are not the same why Pu/U ratios cannot be worked out from these data alone.
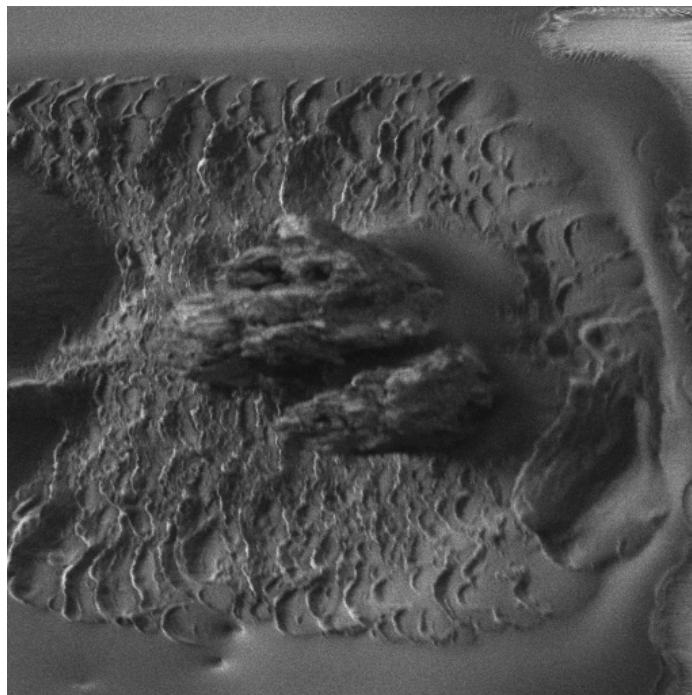
Figure 8. Appearance of the particle used for TOF-SIMS analysis following extensive sputtering for more than 8h. The picture is made up of sputtered electrons in a similar way as during scanning electron microscopy. Even though the soft support (conductive cupper-tape) visibly appears as being heavily eroded the particle itself has only been eroded down to a few micrometer depth. The picture also reveals that the particle was made up of two fragments. They were later separated and analysed separatedly.

The aspect on Thule particle homogeneity has been debated and will probably be a subject for some time to come. It was shown by Ranebo et.al (2007) that the U-isotope signature ($^{235}U/^{238}U$ ratio) as well as the U/Pu element ratio changed with sputtering time (depth) in a particle. From U and Pu Lα X-ray peaks from SEM/EDX similar information of elemental U/Pu variations on the surface could be seen. The data indicated that the particles were inhomogeneous. Similar studies by Lind et.al. (2005) using SEM/EDX however showed no variation of the elemental U/Pu ratio in three studied Thule actinide particles.

Using soft leaching agents, such as water, only the outer layer of a particle is affected. Dissolution progresses slowly and when exposed for only a short time the amount of material leached is very small. If the particle studied should be made up of inhomogeneous material with varying U/Pu elemental ratios as well as a mixture of $^{235}U/^{238}U$ ratios this should be reflected in the analysis of the leached material. The elemental and isotopic ratios obtained from the extesively leached particle 3(3)-6 are shown in Figures 9 to11.
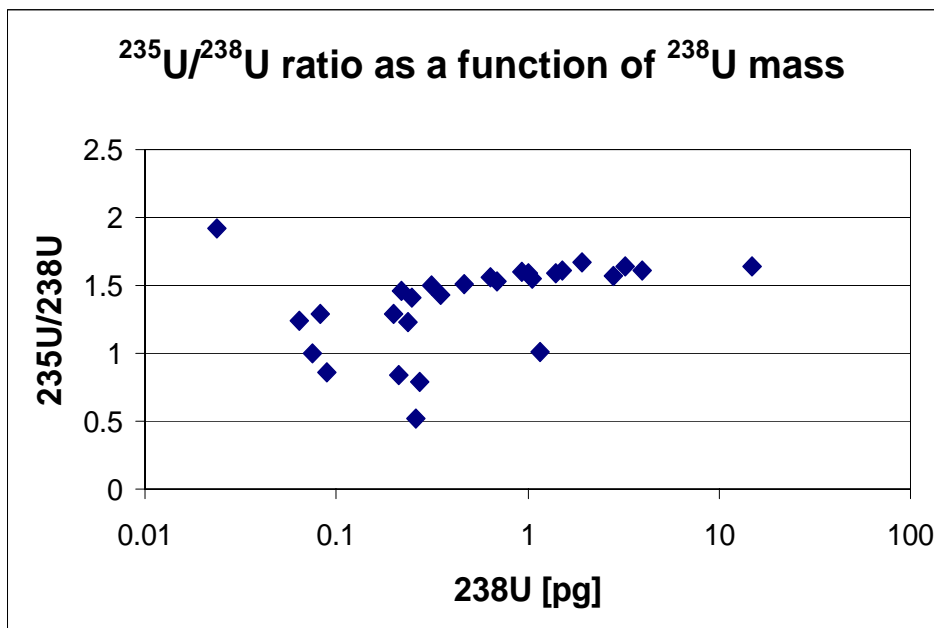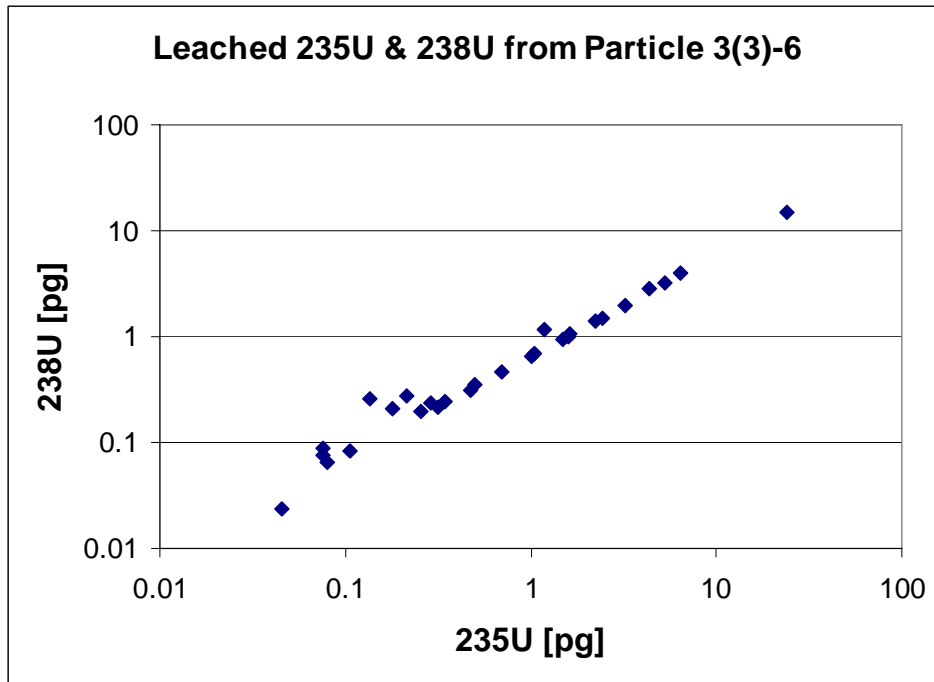
Figure 9. (Top) [235]U and [238]U data from all leaching events of particle 3(3)-6. Apart from a noisy region at low pg-levels the [235]U/[238]U mass ratio is rather constant at around 1.6. (Bottom) The [235]U/[238]U mass ratio as a function of [238]U mass. At lower uranium concentrations influence from background (with natural atom ratios of 0.72%) becomes more and more pronounced.
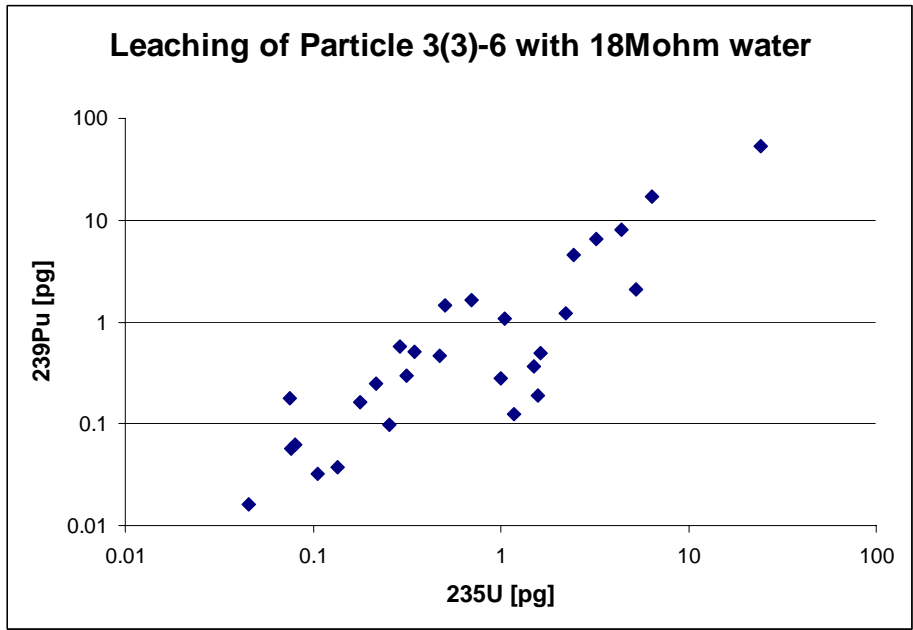
Figure 10. [239]Pu and [235]U data from all leaching-events of particle 3(3)-6. Leaching of Pu and U were not correlated in individual leaching events which indicate that leaching was not simply a mass-transfer process but was dependent on other processes at the surface. For instance redox processes.
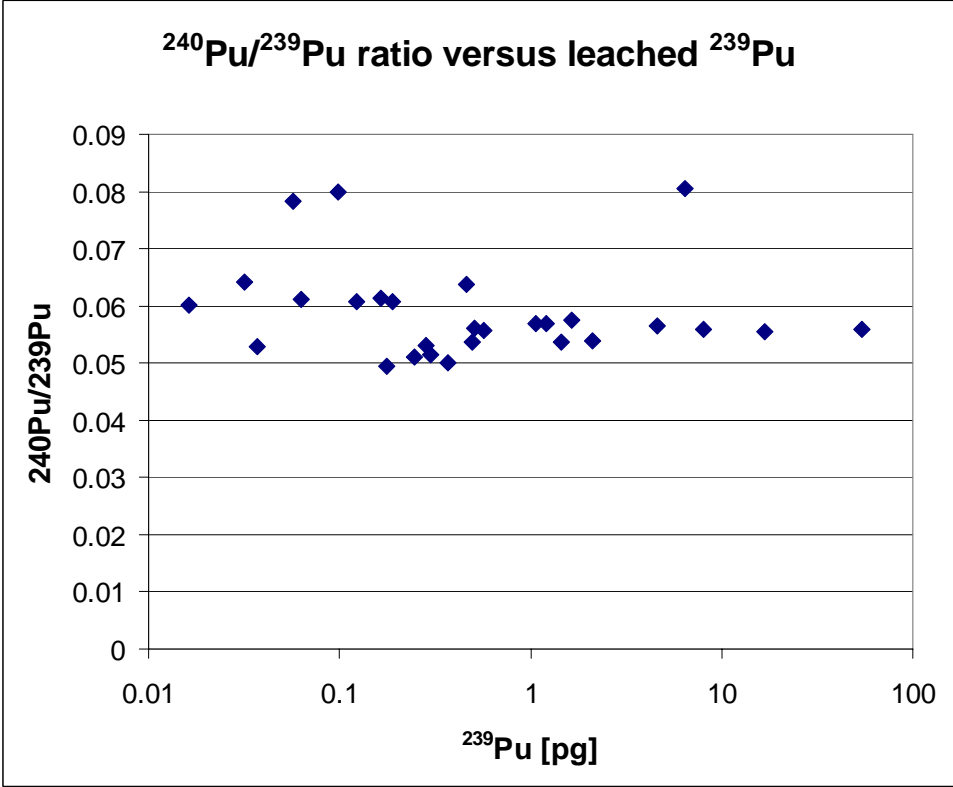
Figure 11. [240]Pu/[239]Pu mass-ratio for all leaching events of particle 3(3)-6. The Thule [240]Pu/[239]Pu source material has been shown in several investigations to have two characteristic atom ratios, 0.056 and 0.027. The particle studied here was an example of the former source.

4.2. Leaching in lung and stomach simulant fluids

For radiological purposes the behaviour of the Thule actinide particles has also been studied when exposed to lung and stomach simulants. The type of experimental set-up of such systems most likely has a major influence on the results and attempts to mimic complicated biochemical reactions should be considered with a portion of humbleness and results seen as indicative. Two completely isolated Thule actinide particles NM-7 and NM-14 with ^{239}Pu activities of 85 and 113 Bq respectively were used for the lung-simulant studies and particle NM-21 with a ^{239}Pu activity of 90 Bq were used for the stomach-simulant study. Activities were determined using the 38.66 and 51.62 keV gamma-lines on a small LEGe-detector with carbon window.

The composition of the lung-simulant was taken from Sdraulig et al. (2008) and given in Table 1.

Table 1. Composition of simulated lung fluid used to leach Thule actinide particles.

Chemical		Concentration [g/l]
Magnesium chloride	$MgCl_2 \cdot 6H_2O$	0.2033
Sodium chloride	$NaCl$	6.0193
Potassium chloride	KCl	0.2982
Sodium hydrogen phosphate	$Na_2HPO_4 \cdot 12H_2O$	0.3582
Sodium sulphate	Na_2SO_4	0.0710
Calcium chloride	$CaCl_2 \cdot H_2O$	0.3676
Sodium acetate	$CH_3COONa \cdot 3H_2O$	0.9526
Sodium bicarbonate	$NaHCO_3$	2.6043
Sodium citrate	$Na_3H_5C_6O_7 \cdot 2H_2O$	0.0970

For the stomach simulant fluid a simplified solution consisting of a 50 mM NaCl solution made to pH 2 with HCl was used. In authentic stomach fluid several other salts are present and also the enzyme pepsin but in these initial tests these were omitted.

Particles were placed in 10 ml Teflon beakers with lid and 100 μl of simulant fluid were added. The beakers in turn were placed in 300 ml plastic containers with water which were placed in a heating cabinet holding 37 ºC. The lung-simulant fluid was exchanged at three intervals during 5 weeks and the stomach simulant twice during one day. Due to risk of adsorption onto container walls during leaching also the Teflon beakers were exchanged during each sampling event. Leached material therefore included acid washing of the Teflon vials. Leaching solutions were analysed using ICP-MS after being screened with a gamma-detector.

Table 2. Results of leaching two Thule actinide particles with lung simulant fluid.

| Leaching time lung simulant	Fraction of Pu leached each time from particles NM-7 and NM-14	
4 days	$9 \cdot 10^{-6}$	$3 \cdot 10^{-5}$
15 days	$6 \cdot 10^{-6}$	$9 \cdot 10^{-6}$
23 days	$5 \cdot 10^{-6}$	$8 \cdot 10^{-6}$
Total in 5 weeks	$\sim 2 \cdot 10^{-5}$	$\sim 5 \cdot 10^{-5}$

Table 3. Results of leaching a Thule actinide particles with stomach simulant fluid. In the second change of fluid the particle disrupted into several fragments when being washed with fresh stomach simulant fluid.

Leaching time stomach simulant	Fraction of Pu leached from particle NM-21
2h	0.003
6h	0.05*

*Particle disrupted.

The results from leaching with lung simulant fluid shows that only a very small fraction of the particle is being 'dissolved'. The fraction $10^{-5} – 10^{-6}$ per day of exposure is about the same order as when leached with water. The experimental conditions are certainly a crucial step in the simulating process. Repreicipitated material onto the particle surface may for instance be a major loss of initially dissolved material. A flow-through container may thus show different results. The set-up of such a device should be such that flow rates around the particle is of the same magnitude as in real lung tissue. In the literature several dissolution studies using lung simulant fluid on uranium oxides of various kinds has been reported. The materials used are often freshly manufactured with no previous long-time exposure to water or other solutions. Results typically show a fast initial leaching in the order of 0.1 d^{-1} but quickly reduces to slow leaching and eventually reaches values in the order of 10^{-4} after some years (Sdraulig et al., 2008). Reports on leaching mixed U-Pu oxides with lung simulant fluids as is the case being studied here is not present in the open litterature. Even it it would, it could not replace site specific information.

The leaching experiments using stomach simulant fluid showed that a large fraction (0.3%) of the particle used could be liberated in only a short time (Table 3). Most likely the low pH facilitates such leaching. Conway et al (2009) measured 0.1-2% and 3-27% loss of Pu in leaching by stomach simulant applied to two groups of Pu-particles isolated from the Semipalatinsk nuclear test site. Clearly the source of the particles is crucial in the leaching behaviour. In the second round of the stomach simulant leaching experiment the particle with some leaching solution was removed from the leaching container with a pipette and placed in a second container for washing. When the fresh washing solution (100 μl stomach simulant) was applied the particle suddenly disrupted into several fragments. The fragments were filtered away using a 0.2 μm filter and later back-flushed to further more closely observe the individual fragments. The filtrate solution was analysed as usual and was shown to hold a large fraction of the particle, around 5%. Possibly in the form of colloidal material passing through the filter. The remaining fragments were placed on a screen to perform autoradiographic analysis. The picture is shown in Figure 12.
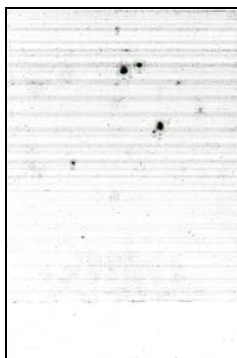
Figure 12. Autoradiographic image of the remains of particle NM-21 after being fragmented

4.3. Evaluating solubility of Thule actinide particles using sequential extraction procedure

Sequential extraction (i.e. the selective dissolution of soil phases with increasingly aggressive chemical treatment) can provide experimental evidence on contaminant partitioning to various soil phases, useful for predicting the mobility and bioavailability of contaminants (Clark et al., 1996). The concept of sequential extractions is based on the idea that a particular reagent is either phase-specific or mechanism specific (Horowitz, 1991). Although each extraction is designed to attack a single geochemical phase, complete specificity is not likely. A major advantage of sequential extraction procedures is that in some degree they simulate the various environmental conditions to which the soil may be subjected (Tessier et al., 1979). All fractions obtained by using selective reagents for the sequential extraction of radionuclides are to some extent only operationally defined. Nevertheless they yield valuable information about relative differences in the association of a radionuclide with soil constituents.

One goal of this work was to obtain information about partitioning of plutonium and americium in Thule actinide particles. Solubility of Pu and Am was evaluated using sequential extraction method. Obtained information may be useful when predicting mobility and bioavailability of other similar particles.

Sequential extraction procedure

Outola et al. (2009) evaluated the sequential extraction procedure developed by Tessier et al. (1979) using two sediment reference materials. Based on the release of ^{239,240}Pu, ^{238}U and stable elements they derived optimum conditions for temperature, concentration and duration. These optimum settings were used in this work and are given in Table 4.

In the first fraction the sediment is treated with $MgCl_2$ to extract relatively soluble species of elements that may be displaced from the solid phase by cation exchange. In the second fraction, ammonium acetate is used to attack easily acid soluble mineral phases. 25 % acetic acid was used to buffer the solution at pH 5 as the release from carbonate phases is affected by changes in pH. In the third fraction, species that are associated with metal oxides and oxyhydroxides are expected to be released when targeted with NH_2OH-HCl in 25% acetic acid. In the fourth fraction, hydrogen peroxide is used as a strong oxidizing agent to release for instance elements associated with organic matter. In the last fraction, nitric acid is used to dissolve all but the most resistant phases. The sequential extraction procedure doesn't release the elements that are associated with more refractory phases such as quartz or aluminosilicates.

Table 4. Sequential extraction procedure (Outola et al., 2009)

Fraction	Reagent used	Temp (^{o}C)	Concentration (M)	Duration (hr)
I	$MgCl_2$ pH 6	25	0.1	1
II	NH_4Ac in 25% HAc (v/v), pH 4	50	1.0	2
III	NH_2OH-HCl in 25% HAc (v/v), pH 2	70	0.1	6
IV	30% H_2O_2 in 0.02 M HNO_3, pH 2	70		3
V	HNO_3	90	4	4

Experimental work

Sequential extraction and isolation of the Thule actinide particles

Two samples (coded as "3" and "4"), each consisting of a single Thule actinide particle in a droplet of water, were received in plastic vials. The particles were transferred from the vial with help of distilled water and isolated by dividing the solution into two portions and determining which portion contains ^{241}Am using gamma spectrometry. This was repeated until the Thule particle was isolated into a water droplet of 30 μl. The ^{241}Am activity of the Thule actinide particle in this water droplet was measured with high purity Ge-detector and results for the both samples are given in Table 5.

The particle in the water droplet was then transferred into a 5 or 10 ml vial and 1 ml of the appropriate reagent at the specified concentration was added to the sample. The vial was placed in a water bath for the appropriate time and temperature as outlined in Table 4 .The procedure for adding the reagent is slightly different for the H_2O_2/HNO_3 fraction. Two reagents were used in this case, 0.05M HNO_3 (0.35 mL) and 30% H_2O_2 (0.55 ml). 0.05 M nitric acid was first added to the sample together with the first portion of H_2O_2 (0.2 ml). The second portion of H_2O_2 was added one hour later and the third H_2O_2 portion 2 hours later.

After each of the sequential extraction step, the Thule particle was isolated into a water droplet and the activity of ^{241}Am in the water droplet was determined with Ge-detector. After the last extraction step (V) when the solution was divided into two portions and measured by gamma spectrometry it was obvious that the Thule actinide particles had disintegrated. The solutions were filtrated through 0.45 μm cellulose nitrate membrane filter and the membrane filters were measured with Ge-detector.

The extracted solutions from the first four steps (I-IV) were acidified with nitric acid and all the solutions were filtrated through 0.45 μm cellulose nitrate membrane filters before radiochemical separations were carried out.

Autoradiograph of the residual material

The membrane filters containing residual material (step V) were also studied by autoradiograph. Figure 13 shows that both Thule actinide particles have been disintegrated into several smaller size particles. The residual from Thule particle "3" contained significant amount of ^{241}Am (3.6 Bq based on gamma measurements, about half of the original activity) while the residual from Thule particle "4" contained only very small amount of activity (0.01 Bq of ^{241}Am and 0.07 Bq of ^{239}Pu based on direct alpha counting, only 0.1 % of the original activity). The approximate size of the membrane filter is demonstrated as a red circle in Figure 13.

a)   b)
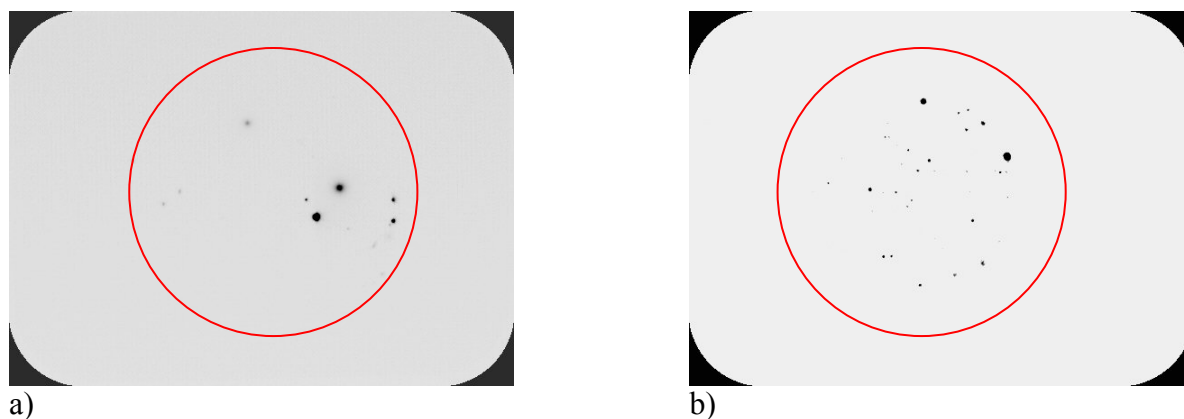
Figure 13. Autoradiograph of the membrane filters containing residual of the a) Thule particle "3" and b) Thule particle "4"

Autoradiograph of the membrane filters used in filtering the extracted solutions
The extracted solutions were filtrated through 0.45 µm cellulose nitrate membrane filters before radiochemical separations. The membrane filters were measured shortly with Ge-detector and no [241]Am was detected. However, since the autoradiograph of the residual material from the Thule particle "4" (fig 13b) showed the presence of small particles even though the activity of radionuclides present in them was very small and below detection limit in gamma measurement, it was decided to measure these other membrane filters also by autoradiograph to see presence of any residual activity not detected by gamma measurements. The images from autoradiograph measurements of all the membrane filters that were used in filtration of the extracted solutions are given in Fig 14. The membrane filters 4II and 4IV showed few hot spots in autoradiograph while the rest of the filters didn't show anything above background. The exposure time was 2-5 days for the autoradiograph measurements. The activity of these two membrane filters (4II, 4IV) is not yet determined by alpha counting but is assumed to be very low, since the gamma measurements didn't show any [241]Am.
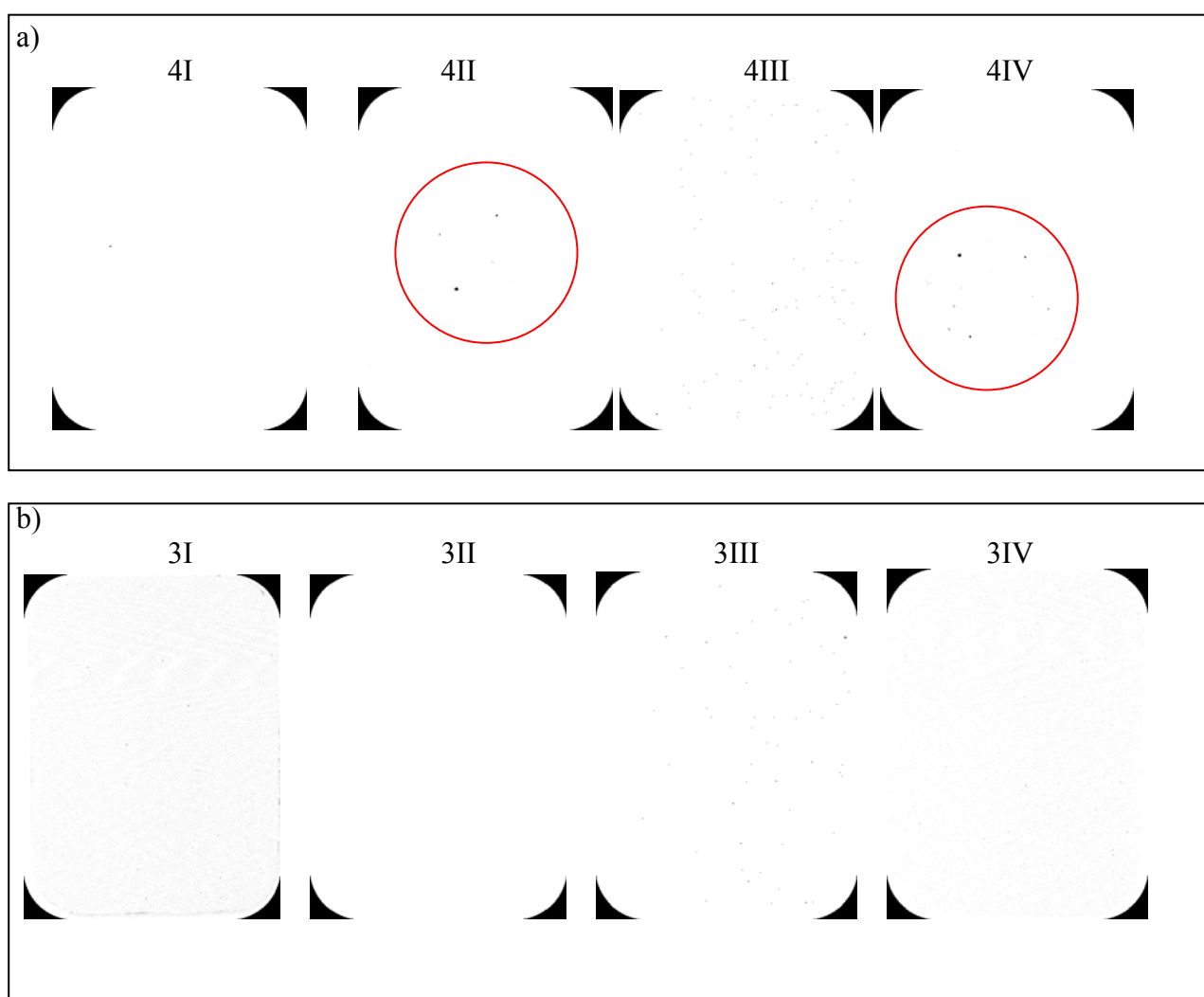
Figure 14. Autoradiograph of the membrane filters used in filtration of the extracted solutions obtained during the sequential extraction of a) Thule particle "4" and b) Thule particle "3". I-IV refers to the steps in sequential extraction procedure that are described in Table 4. The approximate size of the membrane filter is demonstrated as red circles for those two autoradiograph measurements that showed hot spots.

Gamma measurements of the Thule actinide particles

Am-241 activity content was measured from both Thule actinide particles between each extraction. Results are given in table 5. Thule particles were isolated into a single water droplet, size of about 30-50 μm, except in the step V where the particle had disintegrated and the sample solution was filtered through 0.45 μm cellulose nitrate membrane filters and the membrane filter was measured. The exact geometry varied somewhat between the steps because the container that was used in measurements of the first two steps (I, II) were unpractical for handling the particle and the container was changed into a closed Teflon vial for steps III and IV. In the last step (V) residuals of the Thule particles were measured on membrane filters that were placed inside a small plastic vial.

Table 5. Am-241 content of Thule actinide particles (samples "3" and "4") in the beginning and after each extraction step based on gamma spectrometry. Uncertainties are given at 1 sigma but the uncertainty related to changing geometry between the steps is not accounted. Percent of ^{241}Am released in each step is also indicated.

Extraction step	^{241}Am in Thule particle '3' (Bq)	^{241}Am in Thule particle '4' (Bq)	^{241}Am released from the particle "3" (%)	^{241}Am released from the particle "4" (%)
Thule particle in the beginning	7.6±0.5	13.4±0.9		
Step I	7.3±0.4	12.8±0.9	4.18	4.70
Step II	6.5±0.5	11.5±0.8	10.29	9.40
Step III	6.7±0.5	12.0±0.8	0.00	0.00
Step IV	6.5±0.5	5.9±0.4	1.07	42.07
Step V	3.9±0.3	<0.02	37.11	43.82
Left in residual	3.9±0.47	<0.02	47.34	<0.002

Liquid scintillation measurement from the solutions from sequential extraction procedure

A small aliquot was taken from each solution and measured by liquid scintillation to determine total alpha activity present in solutions. This allowed estimating what size of aliquot was needed for Pu/Am analysis. Results are given in Table 6.

Table 6. Total alpha content (Bq) in each extracted solution determined by liquid scintillation counting. Uncertainties are stated at 1 sigma.

Extraction step	Sample '3' (Bq)	Sample '4' (Bq)
Step I	<0.003	0.08±0.01
Step II	0.05±0.01	1.27±0.06
Step III	0.13±0.01	7.58±0.38
Step IV	1.87±0.09	31.3±1.6
Step V	21.2±1.1	47.2±2.4

*Radiochemical separation and alpha measurements*

Based on the gross alpha results from liquid scintillation counting (Table 6), an aliquot was taken from the extracted solutions and spiked with ^{242}Pu and ^{243}Am tracers. A blank sample was also run together with the real samples to determine any possible contamination due to the reagents or glassware. Samples were boiled with HNO_3 and treated with 0.5 ml H_2O_2. Samples were evaporated to dryness and dissolved into 10 ml 8 M HNO_3. After treating the sample with $NaNO_2$, sample was loaded into an anion exchange column (2 ml dowex 1x4, 100-200 mesh) and the column was rinsed with 15 ml 8 M HNO_3. These solutions were collected for ^{241}Am determination. The column was then rinsed with 9M HCl and Pu eluted with NH_4I+9M HCl. Samples was evaporated, dissolved into 2-5 ml 1 M HNO_3. Am and Pu

isotopes were co precipitated by adding 50 µg Ce and 0.5 ml of HF. Solution was then filtrated through 0.1 µm membrane filter and measured with alpha detector for 3-5 days. Example of Pu and Am spectra are given in Figure 15. Co-precipitation of Am from two solutions (fraction I for both samples) did not turn out well. The precipitation in these samples was so large that alpha measurements could not be carried out. These samples contain Mg ($MgCl_2$ was used as a reagent in step I) that probably precipitated with Am. These samples need to be further purified before alpha measurement.

Activity in the residual material (material that was not dissolved during sequential extraction procedure) was measured directly from the membrane filter by alpha counting and the spectrum is shown in Figure 16. The residual from the Thule particle "3" has not yet been measured. Activities of Am and Pu isotopes released from the Thule actinide particles during sequential extractions as well as activities left in residuals are given in Table 7. $^{238}Pu/^{239,240}Pu$ ratio in solutions varied from 0.01 to 0.02 and $^{241}Am/^{239,240}Pu$ ratio from 0.10 to 0.24 respectively.
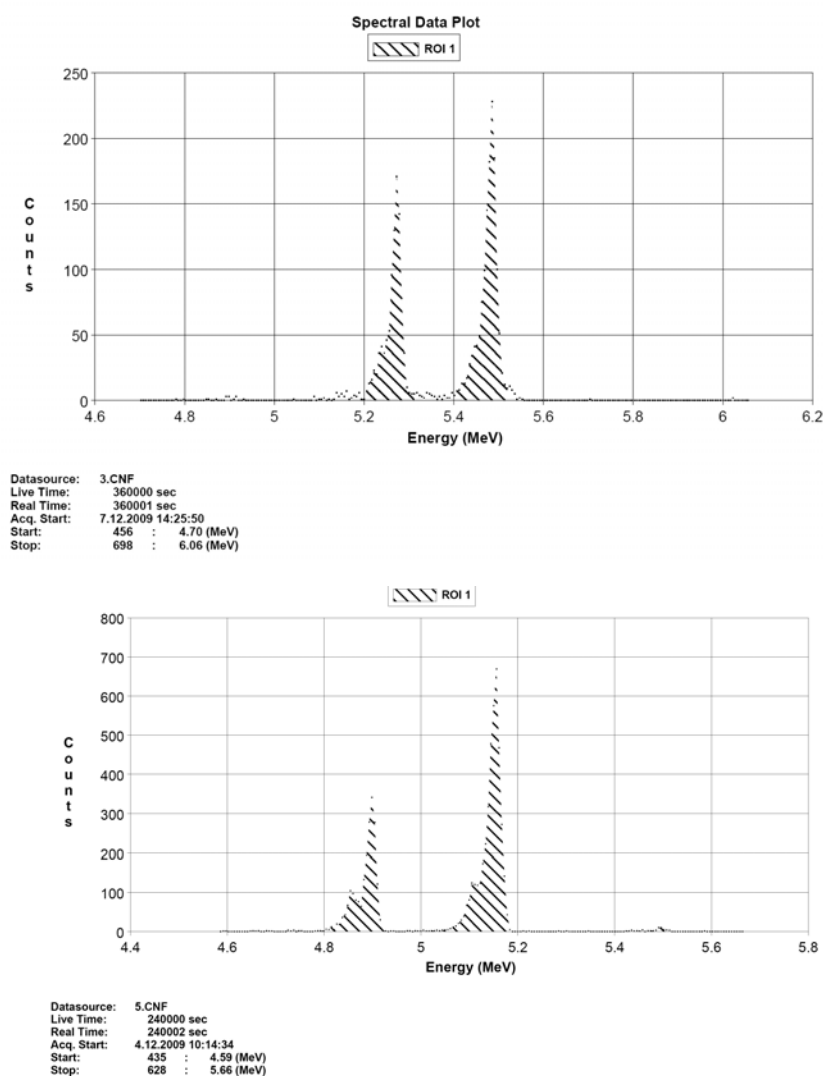
Figure 15. An example of an alpha spectrum of Am (top) and Pu (bottom) spectra after chemical separation.
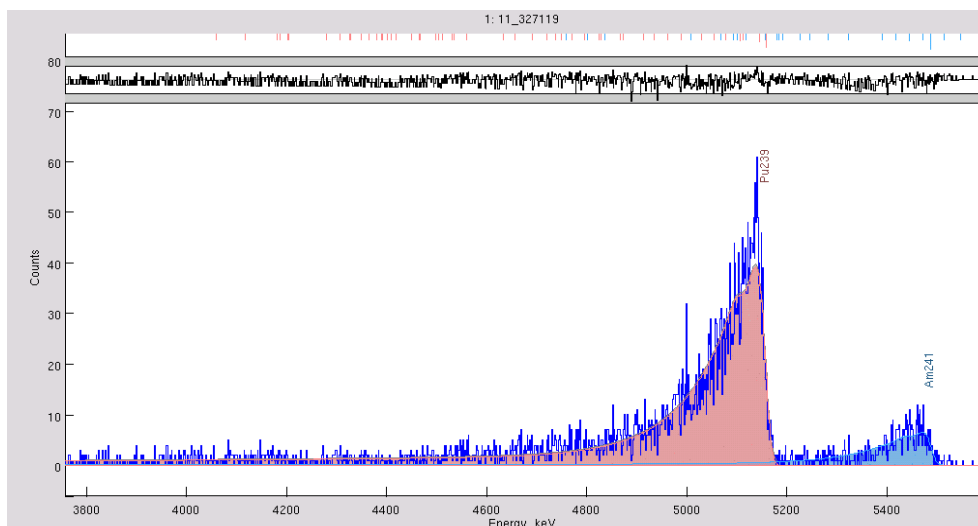
Figure 16. Alpha spectrum of the residual from the Thule particle "4" after sequential extraction was finish, measured directly from the filter without chemical separation.

Table 7. Activities (Bq) of Pu and Am isotopes released in each extraction step during sequential extraction procedure determined through alpha counting. The activity left in residual is also given when determined. Uncertainties are given at 1 sigma.

Extraction step	Sample '3' ^{239}Pu (Bq)	Sample '3' ^{238}Pu (Bq)	Sample '3' ^{241}Am (Bq)
Step I	0.0039±0.0007	<0.001	0.0021±0.0001
Step II	0.031±0.002	0.69±0.28)10^{-3}	0.0078±0.0005
Step III	0.086±0.004	0.0013±0.0002	0.019±0.001
Step IV	1.40±0.10	Not determined	0.41±0.02
Step V	17.5±0.7	0.23±0.04	3.5±0.2
Residual	Not yet analyzed	Not yet analyzed	Not yet analyzed
	Sample '4' ^{239}Pu (Bq)	Sample '4' ^{238}Pu (Bq)	Sample '4' ^{241}Am (Bq)
Step I	0.055±0.003	0.00086±0.00021	0.024±0.001
Step II	1.2±0.05	0.017±0.003	0.15±0.01
Step III	6.5±0.3	0.083±0.013	1.26±0.09
Step IV	26±1	0.28±0.04	6.3±0.4
Step V	42±2	0.53±0.08	6.2±0.4
Residual	0.074±0.003	Not determined	0.012±0.001

Disintegration of the Thule actinide particles during sequential extraction procedure was evident from the autoradiography images collected after the procedure was accomplished (Figure 13). The two Thule particles studied behaved somewhat differently as compared to each other based on gamma measurements, liquid scintillation counting and alpha measurements. The Thule particle '3' started only to dissolve significantly in the last step when the particle was treated with hot nitric acid (fig 17). The residual of the Thule particle '3' contained about half of the original activity. The Thule particle "4" appeared to be more soluble as demonstrated in figure 18. Very small amount of Pu and Am (less than 0.1% for Pu and around 0.2% of Am) was easily exchangeable and released when the sample was treated with $MgCl_2$. Less than 2 percent of plutonium and americium was released when treated with weak acid (fraction II) but already 9 percent of both elements were released under reducing conditions (fraction III). Considerable amount (34% of Pu and 45% of Am) was

released when treated with oxidizing agent, H_2O_2. Most of Pu (56%) and considerable amount of Am (44%) were strongly bound to the particle and were released when treated with nitric acid. Very small amount (0.1% for both Pu and Am) was left in residual, which in the autoradiography pictures showed to have disintegrated into several small particles (Figure 13). Americium and plutonium seemed to behave rather similarly in these experiments.
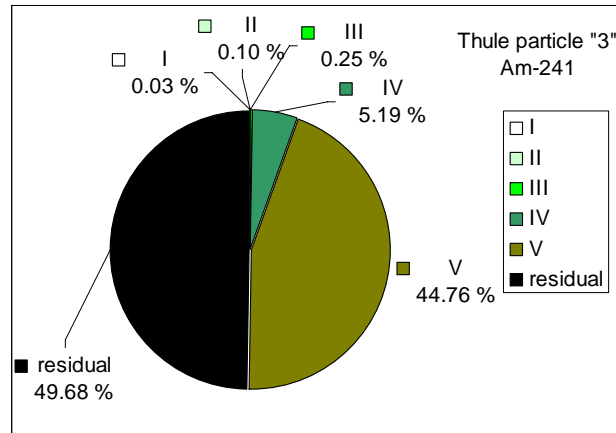
Figure 17. Release of [241]Am (as percentages) from the Thule particle "3" during sequential extraction procedure based on alpha measurement except in residual where [241]Am was determined by gamma. The reagents used in each step (I-V) are given in table 4.
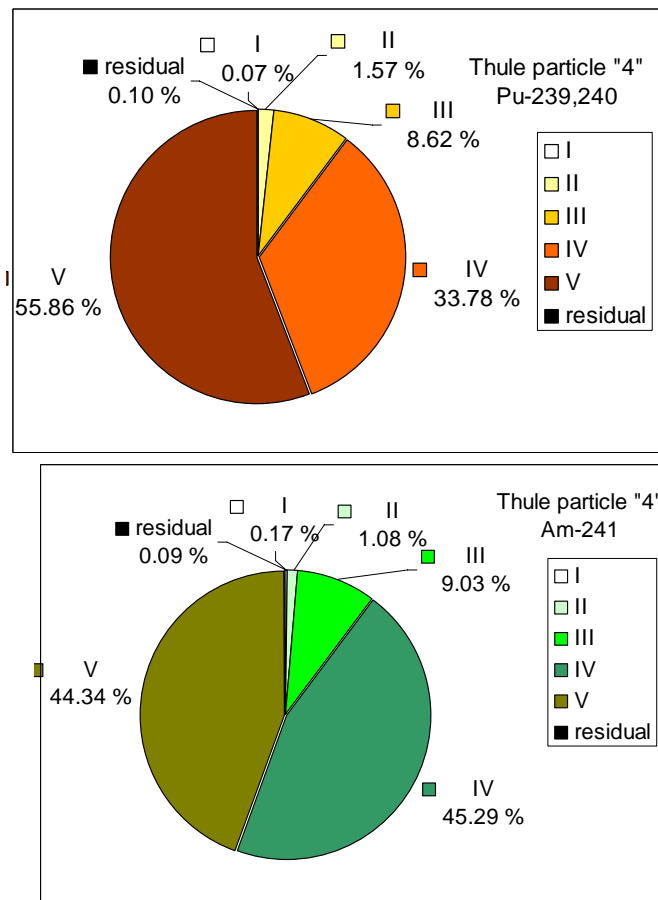
Figure 18. Release of [239,240]Pu (top) and [241]Am (bottom) as percentages from the Thule particle "4" during sequential extraction procedure based on alpha measurement. The reagents used in each step (I-V) are given in Table 4.

5. Characterization of a Thule particle with respect to isotopic and elemental composition

Gamma spectrometry

The gamma spectrometric measurements were done using two different systems: a coaxial high-purity Ge (HPGe) low-energy photon detector (EG&G Ortec LOAX, USA) having a relative efficiency of about 15%, and a resolution of 0.65 keV at 60 keV, and a coaxial HPGe with an ultra-low-background design and Pb-shield (Canberra, Belgium) having a relative efficiency of about 80%, and a resolution of about 2 keV at 1332 keV. The following main peaks were observed: 59.5 keV from ^{241}Am; 129.3 and 51.7 keV from ^{239}Pu. Beside these peaks some additional peaks were observed: 38.8 keV, which at least to some part comes from ^{238}Pu; 43.5 keV from ^{238}Pu/^{241}Am; and 45.3 keV to some part from ^{240}Pu. Additional measurements will be carried out in order to further reveal the origin of the gamma peaks. The count rates of the 59.5 keV peak were in the same magnitude for both detectors.

The LOAX (59.5 keV) was used to verify the presence of the particle in the continuing work of isolating and dissolving the particle.

*Location and isolation of a particle*

Particles were received completely isolated in small vials containing a few microliter of water. The transfer of a particle from one of the vials to a Petri dish was done by adding 100 μl water to the vial, shaking the vial and pipetting the water onto the Petri dish. The particle could be located by using the microscope and transferred by pipette to a small graphite crucible containing 0.1 g LiBO$_2$. The sample was fused at 1050 °C for 10 min. Each step of the transfer and fusion of the particle was controlled by measurements using gamma spectrometry.

Chemical separation and ICP-SFMS measurement

After fusion, the sample was dissolved in 10 ml 1.4 M HNO$_3$. A fraction of the dissolved sample was diluted and a quick scan using ICP-SFMS was performed to assess the approximate concentrations of actinides in the sample.

Two 1 ml fractions of the sample were then used for separations and subsequent measurements. One of the fractions was spiked with an internal standard actinide mix containing ^{233}U, ^{242}Pu and ^{243}Am for quantitative determination of primarily ^{241}Am and ^{241}Pu for age determination of Pu. The separations were done using TEVA, UTEVA and DGA resins as described in Fig. 19. The obtained fractions containing Pu, U and Am were measured using ICP-SFMS (Element2, Thermo Finnigan) equipped with a conical nebuliser and a cyclonic spray chamber ("Twister" – both from GlassExpansion, Melbourne, Australia). The measurements were made in pulse counting mode and the reference material IRMM0731 (IRMM, Geel, Belgium) was used for mass bias determination.

All results were evaluated in accordance with the "Guide to the expression of uncertainty in measurement" (International Organisation for Standardisation, Genève, 1995) and the uncertainties are expressed as the combined uncertainty, *Uc*, with *k*=2.
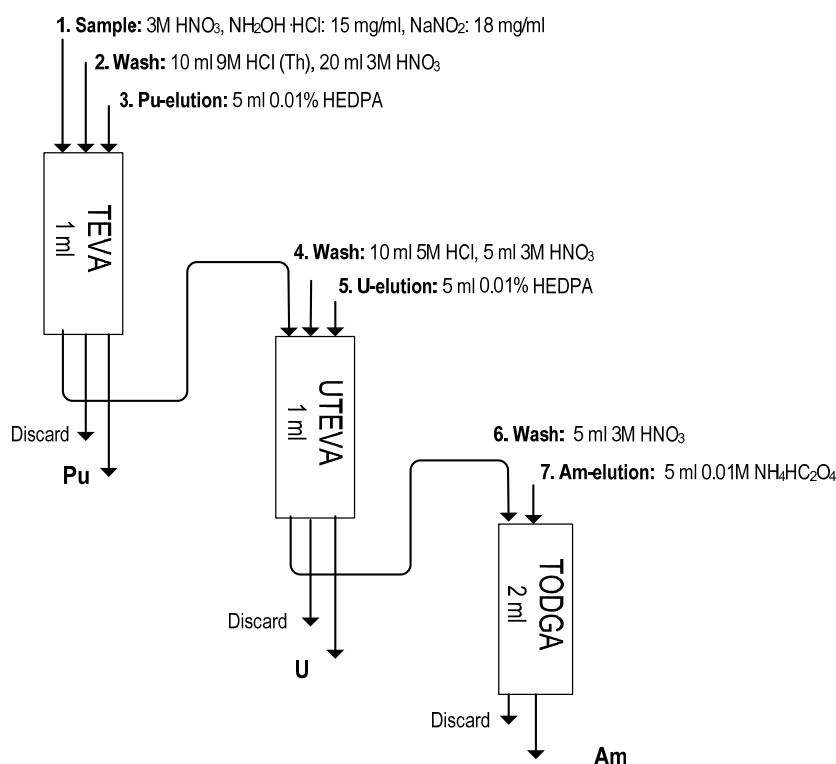
Figure. 19 Chemical separation of U, Pu and Am

Results and discussion of isotopic and elemental measurements
The results of the ICP-SFMS measurements of the particle are shown in Tables 8 and 9. The isotopic ratios of U and Pu are shown in table 8, and it can be seen from the results that the particle consisted of weapons grade Pu and highly enriched uranium. The ratio of [241]Am and [241]Pu was also determined, and from this ratio the age of the Pu in the particle was calculated. The obtained age was 50 y ($Uc = 1$), which is realistic considering that the accident took place 42 years ago. It should however be kept in mind that this value can be biased due to, e.g., insufficient Pu/Am separation in the production of the Pu and eventual fractionation of the two isotopes during and in the time after the release. It was not possible to verify the obtained age by using another ratio (e.g., [236]U/[240]Pu) due to the content of U in the particle.

Table 9 shows the obtained masses of the actinides in the particles. The major actinides in the particle were [239]Pu (24%), [235]U (42%) and [238]U (32%). In the determination of small amounts of U there is always a risk of contamination from environmental U. In the analyses of this particle, the levels of U in the blank was about 26 times lower that in the sample after the whole procedure with dissolution and chemical separation. Hence, the blank levels were not a problem with these analyses. However, the major part of the U blank contribution was from the separation procedure and if lower blank levels are required the volumes used in the separation can be scaled down.

Table 8. Isotopic ratios of actinides in the Thule particle

	$^{240}Pu/^{239}Pu$	$^{241}Pu/^{239}Pu$	$^{234}U/^{238}U$	$^{235}U/^{238}U$	$^{236}U/^{238}U$	$^{241}Am/^{241}Pu$
ratio (n/n)	5.53E-02	3.83E-04	1.47E-02	1.37E+00	5.20E-03	9.68
Uc (k=2)	1.9E-04	1.2E-05	3.7E-05	8.5E-04	2.1E-05	0.44
rel Uc %	0.34	1.5	0.25	0.06	0.41	0.41

Table 9. Mass of actinides in the Thule particle

	^{241}Am	^{239}Pu	^{240}Pu	^{241}Pu	^{234}U	^{235}U	^{236}U	^{238}U
m (g)	9.15E-11	2.44E-08	1.35E-09	9.45E-12	4.69E-10	4.36E-08	1.66E-10	3.31E-08
Uc (k=2)	3.6E-12	8.3E-10	4.6E-11	4.5E-13	1.5E-11	1.4E-09	5.4E-12	1.0E-09
rel Uc %	3.9	3.4	3.4	4.8	3.2	3.2	3.2	3.0

6. Overall Conclusion

This work has been a valuable experience for all parties involved. Techniques in isolating and handling of individual hot particles in the laboratory as well as designing methods for different kind of studies is a challenging subject for material of this kind and the current project has improved these techniques significantly. This has been an important part of the project.

Initial results on leaching of the Thule actinide particles shows that studies using weak solvents are possible to perform on single particles. Experimental setup, blank levels and analytical techniques can be designed so that not only Pu-isotopes and Am may be analysed but also U-isotopes in the particles may be analysed with a minimum of disturbance from environmental material. This means that dissolution of the particle Pu-U matrix can be studied which is a fundamental requirement for understanding particle erosion mechanisms.

The results show that even though the oxide particles are hard to completely dissolve they release material even when exposed to weak solvents like water and salt solutions. Exposures to lung stimulant fluids show relatively slow dissolution rates comparable to what is found using only water. The reason for this is unclear but the answer could be the formation of a secondary surface layer, which is stabilised in the lung stimulant solution. Sequential extraction of particles shows that variation between particles is considerable, some dissolve more easily than the others. Of radiological importance is the disruption of particles when exposed to dissolution as was shown using stomach stimulant solution and sequential leaching. The implication of particle disruption in the environment is an increased surface to volume exposure and thus an increased rate of particle size transfer to smaller particles. If this transformation means a greater abundance of resuspendable particles and if the risk of inhalation of small respirable particles changes due to this is far too early to speculate about. At present lung-dose models incorporating a dynamic change in size (and morphology) of already inhaled particles does not exist but hopefully further studies on these particles will generate data which could stimulate models of this kind.

7. References

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Title	Assessment of weathering and leaching rates of Thule hot particles

Author(s)	Per Roos (1), Iisa Outola (2), Ulrika Nygren (3), Henrik Ramebäck (3), Rajdeep Sidhu (4).
Affiliation(s)	(1)Risoe National Laboratory for Sustainable Energy, Technical University of Denmark (2)STUK-Radiation and Nuclear Safety Authority, Finland (3)FOI CBRN Defence and Security, Sweden (4)Environmental Monitoring Section, Health and Safety Department. Institute of Energy Technology. Norway

Abstract	Within the current project a methodology for separating actinide particles originating from the Thule 1968 accident has been developed. Particles were completely isolated in water using visual and radiometric methods. The particles were attached electrostatic to a plastic support and could easily be moved to any container for leaching studies or other type of studies. Leaching and dissolution studies performed within the project indicate that some particles are relatively easily destroyed or leached while others are more refractory. The results shows that even though the oxide particles are hard to completely dissolve they release material even when exposed to weak solvents like water and salt solutions. Exposures to lung simulant fluids show relatively slow dissolution rates comparable to what is found using only water. Sequential extraction of particles shows that variation between particles is very large; some dissolve easily while some does not. Of radiological importance is the disruption of particles when exposed to dissolution.