EUROPEAN COMMISSION

Community research

COMET

(Contract Number: Fission-2012-3.4.1-604794)

DELIVERABLE 3.4

Final database with description of characteristics of particles

Contributors

R. Garcia-Tenorio (US), O-C. Lind (NMBU), P. Roos (DTU),
C. Sancho (CIEMAT), M. Johansen (ANSTO), I.Vioque (US),
B.Salbu (NMBU) and D.Child (ANSTO),

Reporting period: 15/10/2014– 30/11/2016

Date of issue of this report: 15/01/2017

Start date of project: 01/06/2013 Duration : 48 Months

EURATOM

COMET

DISTRIBUTION LIST

Name	Number of copies	Comments
André Jouve, COMET, EC Project Officer	1	Electronically
Hildegarde Vandenhove, COMET Co-ordinator (WP-1), SCK•CEN	1	Electronically (pdf file)
Contributors: R.García-Tenorio, G Manjón, I. Vioque: (US) O-C. Lind, B. Salbu: (NMBU) P. Roos: (DTU) C.Sancho, Mª Paz Antón, A. Aragón, E. Correa, D.Burgos: (CIEMAT) D.Child, M. Johansen: (ANSTO)	1 per contributor	Electronically (pdf file)
COMET Executive Committee members: WP-1: H. Vandenhove: (SCK•CEN) WP-2: M. Miukku: (STUK) WP-3: Å. Søvik: (NRPA) WP-4: C. Adam-Guillermin: (IRSN) WP-5: B. Howard: (NERC)	1 per member	Electronically (pdf file)
COMET Management Committee: H. Vandenhove: (SCK•CEN) T. Ikaheimonen: (STUK) Å. Søvik: (NRPA) J.Garnier-Laplace: (IRSN) B. Howard: (NERC) A. Real: (CIEMAT) M. Steiner: (BfS) C. Bradshaw: (SU) B. Salbu: (UMB) B. Michalik (GIG) V. Kashparov: (UIAR) S. Gashack: (Chernobyl Centre) K. Nanba: (Fukushima University) P. Masqué: (University of Barcelona) K.O. Buesseler: (Woods Hole Oceanographic Institute) J. Nishikawa: (Tokai University) M. Christl: (ETH, Zurich) R. García-Tenorio: (University of Seville) P. Roos: (DTU) D. Child: (ANSTO)	1 per member	Electronically (pdf file)

COMET Steering Committee	1 per member	Electronically (pdf file)
COMET Wiki site	1 per member	Electronically (pdf file)
ALLIANCE	1 per member	Electronically (pdf file)

Project co-funded by the European Commission under the Seventh Euratom Framework Programme for Nuclear Research &Training Activities		
Dissemination Level		
PU	Public	PU
RE	Restricted to a group specified by the partners of the [COMET] project	
CO	Confidential, only for partners of the [COMET] project	

Table of Contents

1 Background

A major fraction of refractory radionuclides such as Uranium (U) and Plutonium (Pu) released to the environment from the nuclear weapon and fuel cycles is present as particles ranging from sub microns to fragments. Such particles can carry a substantial amount of radioactivity and associated metals, and can act as point sources.

Research indicates that particle characteristics such as composition, atom and elemental ratios depend on the emitting source, while particle size, structure and oxidation states are closely linked to releases scenarios. Following deposition, ecosystem transfer of particle associated radionuclides are delayed compared to mobile radionuclide species; i.e., ecosystem transfer would be delayed until particle weathering and remobilization of associated radionuclides occur. The apparent soil-water distribution coefficient (K_d) will therefore change over time, and the thermodynamic constant concept should be replaced with rate functions.

These particles represent then a significant external and internal radiation risk but there is a high degree of uncertainty in modeling the resuspension, transport, deposition and leaching potential of radioactive particles, and then determining the dynamics of radioactive uptake, exchange and/or transport across ecosystem boundaries. Weathering rates of particles is depending on their composition, structural changes occurring during the release event and local chemical conditions occurring after deposition.

The dynamics of radionuclide transfer of particle-associated radionuclides are often irregular in nature compared with areas where there are no radioactive particles present. Thus, for particle contaminated areas, the overall uncertainty in assessing the health and ecological impacts of radionuclide releases providing accurate and reliable dose assessments, and evaluating the need and options for remediation may be unacceptable high if particle specific parameters are not developed and integrated with existing dose assessment and radionuclide transport models.

The radioactive particles that historically can be found or has been released to the environment can be classified in the following categories (IAEA, 2011).

1.- NORM-particles related to front end of nuclear weapon and fuel cycles (e.g. U-mining)

2.- NORM-particles related to non-nuclear industry

3.-. NORM-particles related to U and Th rich minerals.

4.- Fuel particles, or particles of fissile material formed by mechanical disruption of the original bulk of radioactive material, ranging in size from submicrons to fragments (U/Pu particles)

5.- Condensed particles or molecular aggregates and particles upon condensation of volatile radionuclides

6.- Discrete radioactive particles or clusters formed within the fuel during normal operations or during the release (Ru-particles, activation products).

7.- Colloids or pseudo-colloids either released directly or formed in the environment (1 nm-0.45 μm)

In the frame of the RATE project, the research is focused on hot-particles characteristics, weathering rates, remobilization and prediction of ecosystem transfer of radionuclides associated with U and/or Pu containing particles originating from selected key sources (nuclear weapon tests, safety tests, nuclear reactor accidents, NORM....)(Salbu, 2001), and with this end, a deliverable associated to this research is the creation of a database with the information about identified and isolated hot-particles that potentially are or has been available for performing the transformation studies: biotic and abiotic experiments. The detailed description of this database is covered by this report.

The database is formed by selected isolated hot particles with quite different origin which has been made available by the different partners of the RATE project. This database is not exhaustive, being important to indicate that the partners have in their archives (or has access to) contaminated soil samples from different origin from where they can identify and isolate additional particles if they are needed. But, in spite of this fact, we can indicate that this database is a unique selection of well characterized anthropogenic and naturally occurring nanometre-millimetre size particles representing different historical sources and releases scenarios, which will allow obtaining very rich and original information for prediction of ecosystem transfer of particle-associated radionuclides

2 Localization, identification and characterization of particles

The particles included in this database and available on the frame of the present project have been localized, identified, isolated and characterized using a set of non-conventional techniques in radioecology that will be summarized in the following paragraphs.

All the hot-particles included in the database have been isolated from solid materials (soils, sediments, NORM wastes,….), being used for their localization conventional monitoring/screening techniques for the detection of elevated levels of activity. In this sense, the application of binary separation by using gamma-ray spectrometry and the performance of autoradiographs, have allowed the location and identification of most of them, in some cases using in addition active methods based in the detection of stimulated radiation emitted by the particles of interest when are irradiated with electron beams (application of the electron-microscope technique).

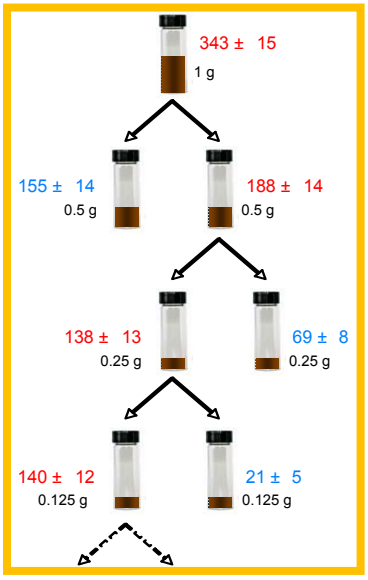


Figure 1:- Scheme of the binary division technique utilized for isolation of particles containing Pu.

After location and identification, the isolation of the particles has been performed in different ways depending of their size and main characteristics. Large particles (in some cases with differentiate colors) have been directly extracted from the bulk material under optic microscope, while for others have been needed the use of micromanipulation systems. Only in few cases, the particle of interest has been characterized with beam based microanalytical methods without its final extraction and complete isolation.

All the particles included in the database have been analyzed, before its complete characterization, by gamma-ray spectrometry (Jimenez-Ramos et., 2010a) as a previous and essential step. Being expected to find in all the particles plutonium in their composition, the signal of ^{241}Am (daughter of ^{241}Pu) have been analyzed and its activity determined, in some

cases together with the gamma-ray emissions of some fission products also present (the presence of fission products in the particle depends of its origin).

The characterization of the particles has been carried out mostly by using microanalytical techniques based in the use of different types of beams (electrons, ions and neutrons). In particular, information about elemental composition has been obtained by analyzing X-ray emissions generated in the particle by the interaction of different beams: X-ray beam (μ-XRF), proton beam (μ-PIXE) and electron beam (SEM-EDX).

The X-rays emitted by the particle are generated in an active/excited volume, with its size being dependent of the beam used because the photons, ions and electrons have different penetration power. In addition, for the same beam, the excited volume depends on the energy. Penetrations of 10-10000 μm, 4-6 μm and 50-70 μm can be obtained with conventional 20 KeV X-rays, 20 keV electrons and 2.5 MeV protons, respectively (IAEA, 2011). On the other hand, the resolution of the information obtained depends of the focalization achieved with the beam: for X-rays the resolutions ranging from 10 nm to μm, for electrons and protons ranging from 1 to 5 μm.

Concerning sensitivity, we can indicate that the limit of detection for particles with thickness until 100 μm will be better for light elements by using μ-PIXE than μ-XRF (due to lower background and high X-ray yields), and clearly better than SEM-EDX (with electron beams, the background is high), while for heavy elements μ-XRF will be comparable or even better than μ-PIXE due to better X-ray yields. For particles thicker than 100 μm the lowest limits of detection are obtained with μ-XRF, because the sensitivity of μ-XRF compared with other microanalytical techniques increase with thickness.

The three microanalytical techniques introduced in the previous paragraphs (μ-XRF, μ-PIXE, SEM-EDX) have been applied by the partnership of this project, for the characterization of the isolated particles forming part of the database. In the great majority the SEM-EDX technique was used, combined with one of the other two techniques. Electron microscopes available for all the partners to perform SEM-EDX, tandem accelerators available at ANSTO and the University of Seville, and synchrotron facilities approached as external users to perform μ-XRF were used. Some additional information concerning these three microanalytical techniques is given below.

SEM-EDX: Using electron beams only superficial information about the composition of the particle and superficial mapping distributions for the different elements can be obtained, Limits of detection are in the order of 0.1 %.

In addition to the microanalysis performed with the electron beam, morphological information can be obtained using additional detectors from images formed by backscattered, secondary and transmitted electrons generated after its interaction with the particle.

μ-PIXE: Proton beams of 1-3 MeV generated by Tandem Van der Graaf accelerators are used. The X-ray spectra generated by the interaction of the proton beam on the analyzed particle, together with the information gained by studying the backscattered protons and their energy distribution (RBS = Rutherford Back Scattering) allow to perform total quantitative scanning analyses obtaining better detection limits than with electrons (1 – 100 ppm) although with low spatial resolution (1 – 10 μm).

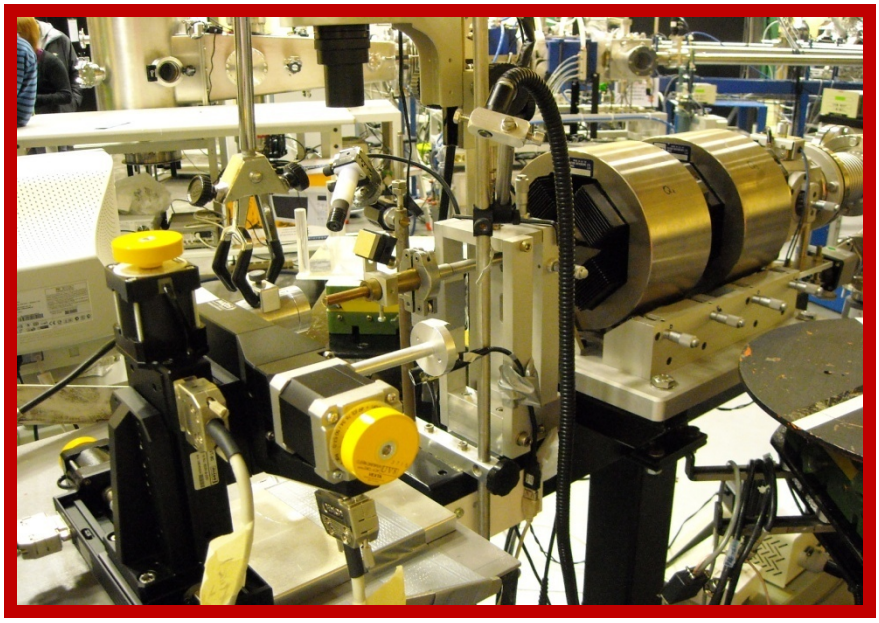


Figure 2

Experimental setup used for μ-PIXE and μ-RBS analyses

The μ-PIXE technique should be considered on the other hand as a semi-destructive microanalytical technique. The incident proton beam can provoke some thermal loading in the interaction volume (with the possible loss of volatile elements) and can "hurt" the incident area by provoking the ejection of some superficial material.

μ-XRF: Through the application of this microanalytical technique, analyses to a greater depth can be achieved due to the more penetrative properties of the beam. In addition, the analyses are possible under ambient conditions and with low thermal loading that allows the measurement of volatile material (Janssens et al., 2000).

μ-XRF can be performed at laboratory scale using typically, as excitation sources, X-ray tubes or radioisotope sources together with focusing and collimating optics to produce the beam, and a detecting system to measure the emitted characteristic X rays from the excited volume of the particle. With proper focusing-collimation, the more advanced systems allow to reach detection limits at the range of several ppm.

Alternatively, X-ray beams enough intense to allow very sensitive microanalysis can be obtained by using much more brilliant synchrotron radiation (electromagnetic radiation from infrared to X-rays) generated by the acceleration of light elements in synchrotron facilities. In the last generation of synchrotron facilities, radiation 10 orders of magnitude more intense

than from the more intense X-ray tubes are provided, being characterized on the other hand the generated beam by a high degree of collimation and for its quasi mono-chromaticity, allowing to obtain very low limits of detection (Salbu et al., 2000).

The use of very intense X-ray beams has additionally the advantage that in addition to μ-XRF other complementary techniques giving structural, morphological and oxidation state information can be applied (Salbu et al., 2001).

In this sense, μ-XRF can be combined with:

a) μ-X ray absorbed near edge structure technique (μ–XANES) to obtain information about oxidation states of elements present in the analyzed particle.
b) μ-X ray diffraction (μ-XRD) to obtain information on structural data in crystalline materials, and
c) μ-X ray computed tomography (μ-XRCT) for the visualization of local structures. This last technique is based in the fact that the intensity of the X-ray beam passing through the sample (the intensity of the transmitted X-ray) depends on density, thickness and elemental composition.

In addition to the microanalytical techniques based in the use of excitation beams, another set of techniques based in atom counting and covered by the general term of mass spectrometry (MS) techniques have been applied. These MS are well-known multi-elemental techniques used for the determination of elemental and isotopic composition and, with basis in their atom counting, provide higher sensitivity and shorter counting times that decay counting methods for long-lived radionuclides determination (Xiaolin and Roos, 2008).

For ultra-trace determinations as the required ones for single micrometer particles, conventional MS techniques are not valid. It is necessary to use techniques such as SIMS (secondary ionization mass spectrometry) or others with intense ion sources (ICPMS, AMS, RIMS). In particular, the best performances are obtained by using intensive ion sources coupled to double focusing systems including electric and magnetic deflection fields.

In inductively coupled mass spectrometry (ICP-MS) aliquots of the sample in dissolution are introduced into plasma and the positive ions are separated by the mass-spectrometer. If the system is coupled with a double (electric/magnetic) sector field (ICP-SF-MS) the mass resolution is highly improved as the interferences and the background are improved. It is possible in optimum conditions to approach sensitivities of ppb (Roos, 2008).

In accelerator mass spectrometry (AMS) low limits of detection can be approached by combining the high sensitivity of mass spectrometers with a high level of discrimination against polyatomic/molecular interferences. In AMS, two mass spectrometers are combined with a particle accelerator that serves as a molecular dissociator, and with sensitive nuclear counters (Fifield, 2008).

In RIMS, selective based resonance ionization in combination with conventional mass-spectrometry allows the determination of trace amounts of long-lived radionuclides. In particular, due to the elemental sensitivity of laser excitation and ionization, on the one hand, and the mass selectivity of the mass-spectrometers on the other, isobaric interferences are removed and high to ultrahigh selectivity can be achieved (Erdman et al., 2008).

Within the frame of the RATE project two main mass-spectrometric techniques (AMS and ICP-SF-MS) have been used for ultrasensitive determination of ^{239}Pu and ^{240}Pu in selected particles. The AMS facilities available at the University of Seville and ANSTO and the high-resolution ICP-MS available at NMBU and DTU have been used. Both techniques (AMS and ICP-SF-MS) are characterized for being destructive techniques: radiochemical isolation of the Pu existing in the particles after their complete dissolution, and conditioning of the Pu isolated fraction to the requirements of the applied MS technique (in dissolution for ICP, as a solid cathode in AMS) is needed. This destructive character imply its application to the selected particles as a final step after their characterization, and for that reason in this report in the majority of cases this information is not provided because the particles are either in the characterization steps before and/or after the biotic/abiotic transformation experiments or subjected to these mentioned studies.

Figure 3

Low-Energy Accelerator Mass Spectrometer (LEAMS) facility at the University of Seville

In addition to the mentioned mass-spectrometric techniques (ICP-SF-MS, and AMS), conventional nuclear techniques (NT), based in detecting emitting radiations, have been used for isotopic Pu characterization in the hot particles (X-Ray spectrometry and Alpha-particle spectrometry). The drawbacks of these nuclear techniques (NT) are the high limits of detection in comparison with the mass-spectrometric techniques (MS), but on the other hand one of them (X-ray spectrometry) is a non-destructive technique that can be applied before the performance of the characterization and transformation studies. Is for that reason because in some of the particles included in the database the Pu composition is known, information that is very important to confirm their source.

In Table 1 are compiled the typical limits of detection values that can be achieved by the different techniques that can be applied for ^{239}Pu and ^{240}Pu determination in particles.

Technique	Limits of Detection
X-ray spectrometry	$10^{2} - 10^{4}$mBq
Alpha-particle spectrometry	10^{-1}mBq
ICP-SF-MS	10^{-2}mBq
RIMS	10^{-2}mBq
AMS	10^{-3}mBq

Table 1.- Limits of detection that can be achieved by using different techniques in the determination of ^{239}Pu and ^{240}Pu in particles (IAEA, 2011)

3 Origin of the radioactive particles forming part of the database

The database compiled in this report is formed by particles made available by the different RATE partners. These particles can be classified in the following groups attending to its origin and/or way of generation.

a) Radioactive particles originating from Nuclear Weapon Tests
b) Radioactive particles from accidental or provoked conventional detonation tests
c) Radioactive particles originating from Reactor Accidents
d) Radioactive particles from accidents in Nuclear Reprocessing plants
e) Radioactive particles collected in NORM sites
f) Radioactive particles generated in TENORM industrial activities

A general description of the particles forming part of each of the mentioned groups is performed in the following paragraphs. Detailed information of the particles forming part of the database is given in the accompanying annex.

a. Radioactive particles originating from Nuclear Weapon Tests

Radioactive particles with origin in the nuclear weapon test sites of Semipalatinsk (Kazakhstan), New Mexico (USA) and Maralinga, Emu and Montebello (Australia) form part of the RATE database.

The Semipalatinsk Nuclear Site (STE) is located in NE Kazakhstan and was the first of one of the main proving grounds for the testing of nuclear weapons by the former Soviet Union. Over the period 1949-1989, a total of 456 nuclear tests were conducted at this site, including 116 atmospheric tests and a number of sub-surface cratering detonations in order to evaluate the potential of using nuclear explosions for civil engineering purposes. A significant legacy of radioactive contamination remains on the surface of the territories comprising the test site and its surrounding (Yamamoto et al., 1996).

A total of 3 isolated particles from Semipalatinsk form part of the database: Two of them were collected in the area called “ground-zero” where high levels of contamination remains due to local fallout associated to the atmospheric tests, while the third one was separated from a bulk soil collected around the crater called “Telkem´2” in an area identified as containing high concentration of transuranic nuclides. The crater “Telkem´2” was produced by 3 low-yield plutonium-fuelled fission devices exploded simultaneously above the ground and is characterized by having an elliptical form (140 m long – 65 m wide) and by being filled with water to a depth of 8-10 m.

The particles isolated from Ground-Zero are representative of the found ones in this area. They are glassy, and vitrified due to the high temperature release scenario and in general contain rather low gamma-activities (Lind, 2006). In addition to transuranics, some fission gamma- emitters of relatively long half-life as ^{137}Cs, ^{60}Co and ^{152}Eu can be detected and quantified.

The radioactive particle from Telkem´2 that form part of the database is also representative of the collected and analysed ones in the area. The Telkem´2 particles appeared to be large grains of soils where U and Pu are distributed at concentrations lower enough to do not possible the detection of these elements with the microanalytical techniques based in the use of excitation beams with higher limits of detection such as SEM-EDX and PIXE (Conway et al., 2007).

Figure 4

View of the crater “Telkem´2” at Semipalatinsk, Kazakhstan.

A couple of small fragments are also available, and form part .of the database, with origin in the 20kT Trinity nuclear weapon test (ground surface shot) carried out in July 1945 near Alamogordo (New Mexico, USA). These fragments (called colloquially as Trinitites) are formed by the melting of products coming or generated in the weapon with dessertic material, being even recently theorized that much of this mineral was formed by sand which was drawn up inside the fireball itself and then rained down in a liquid form.

The Trinity particles, as occurs in most ground surface shots, have an irregular shape, low density, high porosity and concentrations of transuranic and fission products quite diluted in their high dimension. As far as we know, previous to this project no analyses of individual radioactive Trinitite fragments by advanced microanalytical techniques have been published/reported (IAEA, 2011).

We can finally indicate that a total of 8 particles collected at different test sites in Australia form part in the database of the group of particles associated to the nuclear weapon testing program. From 1952 to 1957, the British nuclear weapons testing program conducted 12 detonation tests, called "Major trials" in Australia. Nine of them were conducted in the south of the continent (7 in Maralinga and 2 in Emu Junction) and 3 tests in Montebello Island (see Figure) These tests caused radioactive contamination with nuclear weapons debris, including Pu into the surrounding environment. Most of the contamination was present in particulate form with areas presenting very high number of particles per surface area (Child at al., 2013).

Figure 5

Map of Australia showing the location of the UK weapon test sites

The eight isolated particles (3 from Maralinga, 2 from Emu and 3 from Montebello) are in general relatively large with dimensions in the range 200-800 μm, and their activities in ^{241}Am are relatively low, in the range 0.5 – 5 Bq. Six of them were separated from bulk soils while the remaining two were isolated from shallow sediments in the coast of Montebello islands and have for that reason a marine imprint.

All the particles of the database included in this weapon test group were formed and released to the environment more than fifty years ago and since this time until their collection and isolation particularly their surfaces may have been altered through interactions with the environment (rainwater infiltration, disturbance by wind, water and biological organisms, etc). In the interpretation of the data obtained through the application of different advanced microanalytical techniques it is necessary then to have in consideration and to evaluate the possible role of the ecosystem where these particles have been allocated during the indicated so long interval of time.

b Radioactive particles from accidental or provoked conventional detonation tests

In this section of the database are grouped isolated Pu/U particles with two main different origins but generated/formed in the same way. This group is formed by particles dispersed by accidental explosion/burning of nuclear weapons in aircraft accidents, as well as by Pu particles generated on conventional explosive/burning (i.e. non-nuclear) high-explosive dispersal events performed historically at test sites. Particles from Palomares (Spain), Thule (Greenland) and Taranaki/Maralinga (Australia) form this group.

Uranium and plutonium containing particles dispersed in the terrestrial environment of Palomares, Spain are available for the project, taking the opportunity that following the accident in 1966 of a B52 bomber, and the dispersion in particulate form on the land of the material forming part of the nuclear weapons involved, one of the RATE partners (CIEMAT) has been the national public research body in charge of "Plan for Energy and Environmental Research in Radiation Surveillance in Palomares" that includes the Environmental Radiological Program and the Preliminary Restoration Plan of the contaminated area.

The available Palomares particles were isolated mainly from soils collected in the main different zones (the so-called zones 2 and 3) contaminated each one by the conventional explosion of one of the weapons affected. Quite complete characterization of Palomares radioactive particles have been performed previously by partners of the project (Lind et al., 2007; Aragón et al., 2008; Jimenez-Ramos et al., 2010b). In addition, and for the first time since the accident some particles have been identified and one of them have been characterized from soil material collected in the area called zone 6, a hilly area where the contaminated atmospheric plume formed during the accident interacted, after its transportation by the dominant winds, provoking the deposition of some suspended material.

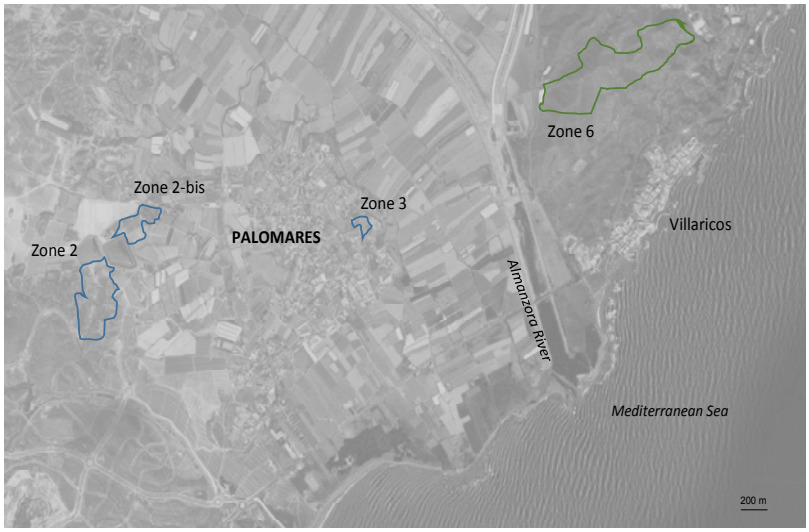


Figure 6

Map of Palomares, showing the different contaminated zones from where the particles were isolated

On the other hand, following a similar B52 accident in 1968 at Thule (Greenland), and the dispersion in particulate form on the sea and on the land of the material forming part of the nuclear weapons involved, a lot of expeditions and studies have been carried out in the area, mostly by one of the partners (DTU). This partner has previously isolated and characterized hot particles from the affected area (Eriksson, 2002) and has made available for the transformation studies performed in RATE, selected hot particles mainly from terrestrial origin. NMBU has also performed previous studies characterizing particles from Thule with marine origin (O.C.Lind et al., 2007) located within the sediments of Bylot Sound.

The number of particles isolated from the Palomares and Thule scenarios and included in the database is elevated due to the special interest in the project to perform comparative evaluations of transformation biotic and abiotic experiments, because both cases are characterized for similar source-similar accident and release scenario, but they have been residing for 50 years in very different environmental compartments. In both cases the B52 bombers carried thermonuclear bombs and crashed after fire in the plane. In both cases the bombs detonated conventionally with a subsequent explosive fire, dispersing micrometer particles where enriched U and weapon grade Pu coexist, but in a non homogeneous mixture (surface inhomogeneities in both Palomares and Thule particles were observed (O.C.Lind et al., 2007)). In both cases the particles are characterized by low $^{239}Pu/^{235}U$ (0.62-0.78) and $^{240}Pu/^{239}Pu$ (< 0.07) atom ratios, and in both cases the particles have similar morphology (are particles with high porosity and very fragile (Figure 7). From the studies performed until now, it seems that particle characteristics are apparently more dependent on the source and the release scenario than from the environment where the particles have been disposed over time.

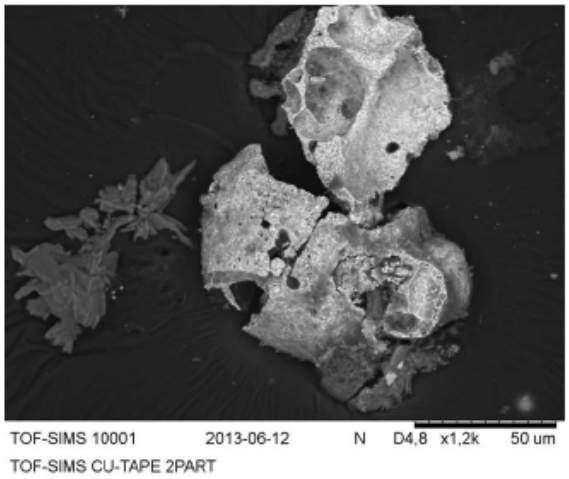


Figure 7

TOF-SIMS images of Thule particles showing clearly their fragility

The particle matrices in both cases are U and Pu oxide mixtures (the original metallic U and Pu in the bombs was oxidized in the explosive fires) and their persistence during 5 decades is an indication of its in general inert behavior under the existing conditions. The evaluation of this inert behavior and the confirmation of possible increments in their solubility over time is one of the objectives to be analyzed on the frame of RATE project.

The set of Palomares and Thule particles are complemented with two Pu particles isolated from soils collected at Taranaki site, Maralinga (Australia) where 12 non-nuclear explosion tests ("Minor trials") were performed at the beginning of the 1960´s. These tests dispersed more than 22 kg of Pu, resulting in four radioactively contaminated deposition plumes radiating from the test site (Johansen et al., 2014) in a way similar to the occurred one accidentally in Palomares and Thule. Is for that reason of special interest to compare the results obtained: a) in the characterization of the particles (composition, morphology, chemical forms, oxidation states…), and b) in the abiotic/biotic experiments performed with them.

c Radioactive particles originating from reactor accidents

It is a well-known fact the dispersion in the environment of radioactive particles with origin in the Chernobyl accident (Kaspharov et al., 2003). In fact, and for several years the presence of radioactive particles was referred to as a peculiarity of the Chernobyl accident, without to have in consideration the formation of particles in previous source and released scenarios (weapon tests, releases of nuclear reprocessing plants…)

The radioactive particles associated to the Chernobyl accident can be classified in a simple way in three main groups as follows (IAEA, 2011):

a) The group known as the ruthenium particles because just after the accident the ^{103}Ru and ^{106}Ru isotopes were the dominant gamma emitters. In addition, these particles mainly contain transition metals and other radionuclides such as ^{60}Co and some volatile elements while do not contain or has little uranium (Pollanen, 1997).
b) The group known as the fuel particles. These particles are U oxide fuel fragments containing a range of fission and activation products found in the irradiated fuel and being depleted in gases and volatile elements (Salbu, 2000; Salbu, 2001). They contain also transuranics (Pu, Am and Cm) and some beta emitters such as ^{90}Sr and ^{90}Y (Broda et al.,1989).
c) The group known as condensation particles (Viktorova et al., 1993). This third group of radioactive particles found in the environment was formed by condensation of the volatile elements on secondary particles such as aerosols and soil components. No Pu and U is present in these particles that are on the other hand the major components of the long-range transport and deposition.

Within the frame of this project we are interested in the uranium fuel particles (U/Pu) collected in the vicinity of the damage reactor, which can be classified in two sub-groups according to its shape and its geographical location. Irregular shaped fuel-like radioactive particle were formed by the initial explosion, when mechanical destruction of fuel occurred and fuel particles were deposited to the west of the reactor. More spherical particles were produced in-situ in the subsequent burning fuel and transported to the north.

To assess the long-term consequences in its environmental behavior, information on the commented source and release dependent characteristics of the particles is needed. The irregular shape particles initially released due to mechanical explosions to the west are mainly formed by metallic U and UO_2 with the uranium in reduced form, having as a consequence an inert behavior (being expected slow rates and delayed ecosystem transfer) while the particles released in the subsequent fire to the north were oxidized (being expected more rapid weathering rate and rapid ecosystem transfer) (Salbu, 2000) (Lind, 2006).

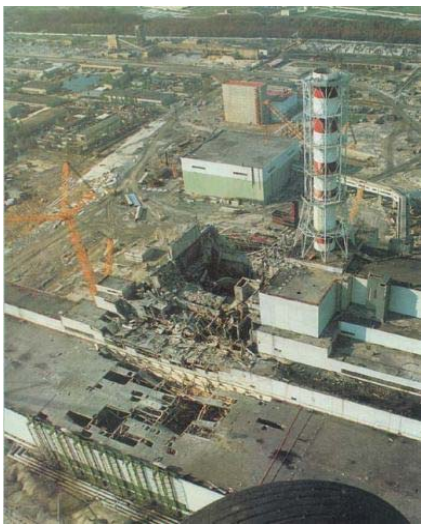


Figure 8

Photo showing the magnitude of the Chernobyl accident

NMBU as a recognized leader in the field of analysis and characterization of radioactive particles, and with long experience in the analysis of Chernobyl U-fuel particles by applying modern microanalytical techniques are providing from their archives Chernobyl particles coming from the two commented affected areas (west and north) (Salbu, 2000; Salbu et al., 2001; Lind, 2006).

U/Pu particles associated to the Fukushima accident?

An open question which has created some controversy in the last months is the possible release to the environment of fuel (U/Pu) radioactive particles from the Fukushima Reactors.

After severe nuclear events, a major fraction of refractory nuclides such as U and Pu are released to the environment in the form of radioactive particles. After the Fukushima Daiichi Nuclear Power Plant (FDNPP) accident, Pu isotope ratio signals different from that of global fallout have been reported, indicating that spent fuel particles could have been released from the reactor or reactor vessels. However, although the presence of radioactive particles originating from the fuel is expected, confirmation is still needed because to date no spent fuel particles in the FDNPP surroundings have been identified (Salbu and Lind, 2016).

In the surroundings of the FDNPP, radioactive particles containing ^{137}Cs and other volatile nuclides as well as a series of stable refractory elements (Cs, Fe, Zn, U, etc) have been

identified by several authors (Abe et al., 2014). But these particles cannot be originated from the FDNPP fuel, because in that case long-lived radioactive isotopes of the refractory metals should have been identified in these particles. Measurement of long-lived fission or activation products (e.g Fe and Zn isotopes) or transuranics (^{236}U:^{238}U; ^{240}Pu:^{239}Pu) atom or isotope ratio signals reflecting burn-up are needed to identify particles originating from the fuel. It is therefore most probable that volatile radionuclides released as gases during the accident have deposited on available surfaces such as fly-ash, forming condensation particles during release and/or transport.

d Radioactive particles from accidents in nuclear reprocessing facilities.

Particles have also been released to the environment associated to accidents in nuclear reprocessing plants. Radioactive particles associated to Sellafield (Salbu et al., 2004), Dounray (Jaeschke et al., 2015), Mayak (Salbu, 2001), etc have been reported.

In particular, the Dounray nuclear site (north coast of Scotland) was responsible for the release of an unknown quantity of particles and fragments of irradiated nuclear fuel during the 1960s and the 1970s. These Dounrey radioactive particles were either produced as a result of fault conditions during milling and cropping operations or during incidents in the dissolution cycle during reprocessing and they were dispersed on the Dounrey foreshore (Dennis et al., 2007).

The population of Dounrey particles released to the environment is dominated by the so called Materials Test Reactor Particles (MTR) and the Dounrey Fast Reactor Particles (DFR).

The MTR particles are originated at Dounrey during the preparation for reprocessing of various kinds of MTR fuels from a number of reactors around the world. The MTR particles consist mainly of Al with some inclusions of an Aluminum-enriched uranium alloy. The MTR particles contain actinides and fission products as the result of the irradiation of the fuel in the reactors and include ^{137}Cs and ^{90}Sr but do not contain ^{60}Co and ^{94}Nb.

The DFR particles are primarily composed of U and Nb with associated actinides and fission products and are formed from enriched uranium fuel encased in a niobium metal cladding. Particles of DFR may be distinguished from those of MTR by the presence of ^{94}Nb, but the absence of ^{94}Nb is not conclusive, since ^{94}Nb might be present at levels below the limit of detection. In this case, to distinguish between DFR and MTR particles, SEM/EDX technique can be applied for the identification of Nb in the DFR particles and Al in the MTR particles.

In the database of the RATE project two particles of Dounrey are included, being provided by NMBU. One of the particles is from the MTR group and the other is a DFR particle.

e Radioactive particles from NORM/TENORM sites

The presence of radioactive particles in the environment has been generally associated to their releases from nuclear sources including nuclear weapon tests, accidents with nuclear weapons, reactor accidents and accidents from reprocessing plants, as it has been shown in this report. Radioactive particles existing in the environment from NORM (Naturally Occurring Radioactive Materials) sources, with few exceptions, have been much less in focus, although the failure to recognize the presence of these particles in an ecosystem can have a number of serious consequences with independence of the nuclear origin or not of these particles. The presence of insoluble particles in bulk samples may cause incomplete dissolution of samples leading to analytical inconsistences, erratic conclusions and unacceptably large uncertainties associated with predictions for dispersion and ecosystem transport as well as dose assessment (Salbu et al., 2004) (IAEA (2011).

The possible sources of NORM particles are huge around the world, being present either in unperturbed areas enriched in radionuclides of Uranium and/or Thorium series or in contaminated areas by the releases of wastes generated in conventional industries that treat NORM raw materials (these wastes are commonly known as TENORM: Technologically Enhanced Naturally Occurring Materials).

Within the frame of the RATE project, were available for the transformation studies a good number of particles from different NORM/TENORM sites. In particular:

a)The database is enriched by a couple of particles isolated from a alum shale formation in Norway. The alum shale formation is a formation of black shale containing pyrite, found in southern Scandinavia that in its decomposition by weathering forms sulphuric acid which acts on potash and alumina constituents to form alum. The alum shale contains enriched levels of Uranium with their daughters in secular equilibrium (in fact, between 1950 and 1989 Sweden used alum shale for Uranium production), being in the alum shale formation the U levels quite heterogeneous due to the presence of U inclusions in some particles or fragments (Skipperud et al., 2016).

The two alum shale particles have been provided by NMBU, isolated from the ore material extracted in the process of construction of a tunnel (RV4) at Gran, Hadelend, Norway.

b)Ten particles have been isolated, and were available for the transformation studies, from soils collected in an undisturbed naturally Th-rich site. This site is located in south of Norway, called Fen/Sove, forming part of a complex of alkaline rocks and carbonates enriched in rare earths, niobium and thorium (Popic et al., 2014). As soil radionuclide concentrations are determined by those in the parents materials and by physical and chemical phenomena, the Fen/Sove soils were shown to have significantly elevated ^{232}Th and moderate ^{238}U concentrations. However, and associated to their origin, the ^{232}Th distribution in the soils is not uniform, being possible to observe particles/fragments with inclusions of this radionuclide. Some of these particles are forming part of the RATE database.

c)A couple of particles have been also provided by NMBU from U mining areas of Central Asia (Lind et al., 2011). Following the cold war, extensive U mining and production took place at selected sites in Central Asia as a vital part of the nuclear weapon program in the former Soviet Union. In these areas all types of Uranium recovery were undertaken: open-cast extractions, underground mining, in-situ leaching with sulphuric acid solutions, etc.

In soil samples collected at the abandoned U-sites in Kazakhstan, Kyrgyzstan and Tajikistan the heterogeneous distribution of radionuclides and metals have been demonstrated (Lind et al., 2013) based on soil autoradiographs. The two particles were particularly isolated from soils collected at the former U site at Kadji Sai, Kyrgyzstan after their identification and characterization using micronalytical techniques, searching for information on the solid state speciation of uranium and other metals which can improve the basis for assessing environmental impact of TENORM activities.

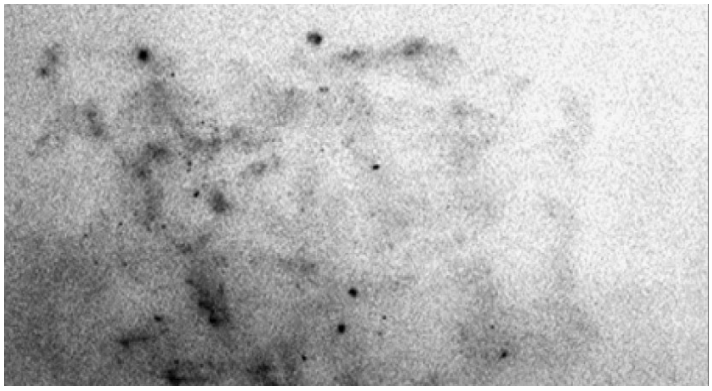


Figure 9

Autoradiography of a soil sample from the former U site at Kadji Sai, Kyrgyzstan showing the presence of radioactive particles

d)In addition, several U particles were isolated along the production process of a phosphoric acid plant located in Huelva, South West of Spain and provided to the database by USEV. In this paradigmatic NORM industrial activity are treated phosphate rock minerals enriched in uranium with their daughters in secular equilibrium.

The particles included in the database were isolated from waste material accumulated/generated in the digestion and filtration units of the plants (Bolivar et al., 2009), and should be reflecting inclusions of U in the original raw mineral that due to its refractory behavior are not dissolved in the production processes (García-Tenorio et al., 2015). These U particles have a well defined crystallization structure with sizes variable but always at the micrometer level.

e)Finally, the RATE database has been completed with different monazite particles isolated from soils collected in the center of Spain. In a mining area, called Matamulas, and located 200 km southern Madrid (Spain), pilot studies are under development to evaluate the possible extraction of monazite mineral enriched in rare-earths. This monazite is present in granular forms, as particles of 1 mm- 1.5 mm size, high density and hardness, and are diluted in mass in the soils in concentrations in the interval 1-2%. These particles are located at superficial level (1-2 m) due to its alluvial origin, and present high levels of ^{232}Th and moderate concentrations of ^{238}U.

Figure 10

Filtration Unit of a Phosphoric Acid Plant where can be found radioactive particles

The physical and morphological characteristics of these particles together with the difficulties observed in the laboratory for their dissolution even after the application of very aggressive dissolution processes, gives evidences to hypothesize its inert behavior in the environment and associated extremely low weathering rates. This fact it is important to be ratified through the application of the transformation procedures applied within the frame of the RATE project (García-Tenorio et al., 2016).

4 Summary

Selected radioactive test particles have been made available from all partners, following collection and isolation from environmental samples. In this report, information about the database created with the knowledge obtained from these particles, is included. Characterization of particle properties or particle associated radionuclides using advanced solid state speciation techniques as well as atom ratio/isotope ratio/element ratio determinations have been performed as a basis to gain information about weathering rates, remobilization and prediction of ecosystem transfer of radionuclides associated with U and/or Pu containing particles originating from selected key sources (nuclear weapon tests, safety tests, nuclear reactor accidents, NORM....). The information gained will allow decreasing the uncertainties of integrated dynamic models assessing long-term environmental impacts which take into account the source-term, transport and deposition, mobility and biological uptake and accumulation. In addition, this database covering known events can be utilized for evaluating consequences for future events (Salbu, 2016)

In the characterization of the particles forming part of this database, the following highly advanced technologies have been applied.

a) To demonstrate heterogeneous distributions of radioactivity in samples: **Autoradiography by P-imaging and/or gamma measurements**

b) To determine size distributions, particle morphology, 2D surface elemental distributions and as a preparatory mean for further micro-analytical experiments.: **ESEM/SEM/TEM interfaced with EDX**

c) To obtain and quantify vertical and horizontal elemental distributions and elemental ratios: **μ-PIXE**

d) To obtain 2 and 3D information on elemental distributions, crystalline structure/density: and oxidation states: **μ-XRF,: μ-XRD, μ-XANES using synchrotron radiation x-ray microtechniques** at facilities in Germany (PETRAIII), France (ESRF), and Australia (AS),

e) To obtain 3D density distributions: **X-ray absorption nanotomography (nano/micro-CT)** ,

f) To quantify concentrations and isotope ratios of radionuclides in total samples as well as fractions: I**CP-MS**

g) To obtain 2D surface elemental distributions: **LA-ICPMS**

h) To perform imaging and speciation of particles: **TOF-SIMS** , and

i) To quantify concentrations and isotope ratios of radionuclides in total samples as well as fractions: **AMS**

Previous research performed by the RATE consortium indicate that particle characteristics such as composition, isotope or atom ratios depend on the emitting source, while characteristics such as structure and oxidation states are closely linked to the associated release scenarios. Furthermore, weathering processes depend on both physical and chemical particle characteristics such as the morphology, structure, mechanical rigidity, particle size and the oxidation state of the carrying matrix. For that reason, transformation studies (biotic and abiotic laboratory experiments) are being performed in selected particle samples that include those from: a) Nuclear weapon tests, b) Conventional detonation of nuclear weapons, c) Reactor accidents, d) Accidents in nuclear reprocessing facilities, e) NORM sites with unprocessed radionuclides, and f) NORM sites at which the radioactive materials have been processed.

The information about the number and origins of the particles that are included in the database created, and consequently that potentially are available for the projected transformation studies, is compiled in the following Table.

Origin of the Particles	Number of particles
Nuclear Weapon Tests	12
Conventional detonations	21
Accidents in Reactors and Nuclear Reprocessing Plants	8
Reactor Accidents: Chernobyl	3
NORM Sites	10
TENORM facilities	8

Table 2.- Origin and number of radioactive particles included in the database

References

Abe, Y., Iizawa, Y., Terada, Y., Adachi, K., Igarashi, Y., Nakai, I. (2014). Detection of uranium and chemical state analysis of individual radioactive microparticles emitted from the Fukushima nuclear accident using multiple synchrotron radiation X-ray analysis. *Anal. Chem* 86, 8521-8525

Aragón A., Espinosa A., De la Cruz B., Fernández J.A. (2008). Characterization of radioactive particles from the Palomares accident, Journal of Enviromental Radioactivity 99, 1061-1067.

Bolívar JP., Martin JE., Garcia-Tenorio R., Mas JL. (2009). Behaviour and fluxes of natural radionuclides in the production process of a phosphoric acid plant. *Applied Radiation and Isotopes* 67, 345-356.

Broda, R., Kubica, B., Szeglowski, Z., Zuber, K., (1989) Alpha Emitters in Chernobyl HPs. *Radiochimica Acta* 48, 89-96.

Child D.P., Hotchkis, M.A.C. (2013) Plutonium and uranium contamination in soils from former nuclear weapon test sites in Australia. *Nuclear Instruments and Methods in Physics Research, part B*, 292, 642-646.

Conway M., León-Vintró L., Mitchell P.I., García-Tenorio R., Jimenez-Ramos MC. (2007) In-vitro analysis of the dissolution kinetics and systemic availability of plutonium ingested in the form of hot particles from the Semipalatinsk NTS. *Applied Radiation and Isotopes* 67, 884-888.

Dennis F., Morgan G., Henderson F. (2007) Dounreay hot particles: the story so far. *Journal of Radiological Protection* 27, A3-A11.

Erdmann, N., Passler, G., Trautman, N., Wendt, K., (2008) Resonance ionization mass-spectrometry for trace analysis of long-lived radionuclides. In *Radioactivity in the Environment*, Elsevier pp 331-354

Eriksson M., (2002). Weapons plutonium in the Artic environment (Thule, Greenland). Riso National Laboratory, pp 1-146.

Fifield, L.K., (2008) Accelerator Mass Spectrometry of Long-lived Radionuclides. In *Radioactivity in the Environment*, Elsevier pp 263-293

García-Tenorio, R. et al. (2015). Management of by-products generated by NORM industries: Towards their valorization and minimization of their environmental radiological impact. Journal of Radioanalytical and Nuclear Chemistry 306, 641-648.

García-Tenorio, R. et al. (2016) Radiological evaluation associated to the mining of monazite in Central Spain. In Book of proceedings 8th International Symposium on naturally Occurring Radioactive Material-NORM VIII, Rio de Janeiro, in press.

IAEA (2011) Radioactive Particles in The Environment: Sources, particle characteristics and Analytical techniques. IAEA-TECDOC-1663, IAEA, Vienna, p.90

Jaeschke, B.C., Lind, O.C., Bradshaw, C., Salbu, B. (2015). Retention of radioactive particles and associated effects in the filter-feeding marine mollusc Mytilus edulis. *Science of The Total Environment* 502, 1-7.

Janssens, K., Adams, F., Rinsby, A. (2000) Microscopy X-Ray Fluorescence Analysis, J. Wiley & Sons Ltd.

Jimenez-Ramos MC., Hurtado S., Chamizo E., García-Tenorio R., Mitchell P.I., León Vintró L. (2010) ^{239}Pu, ^{240}Pu and ^{241}Am determination in hot particles by low-level gamma spectrometry . *Environmental Science and Technology* 286, 557-563.

Jimenez-Ramos MC., Eriksson M., García-López JL., Ranebo Y., García-Tenorio R., Betti M. and Holm E. (2010) A comparison of two micro-beam X-ray emission techniques for actinide elemental distribution in microscopic particles originating from the hydrogen bombs involved in Palomares (Spain) and Thule (Greenland) accidents. *Spectrochimica Acta, Part B* 65 (2010) 823-829.

Johansen, M.P., Child, D.P., Davis, E., et al (2014) Plutonium in wildlife and soils at the Maralinga legacy site: persistence over decadal time scales. *Journal of Environmental Radioactivity* 131, 72-80

Kaspharov, V.A. et al. (2003) Territory contamination with the radionuclides representing the fuel component of Chernobyl fallout. *The Science of the Total Environment* 317, 105-119.

Lind O.C. (2006) Characterisation of radioactive particles in the environment using advanced techniques. Thesis. ISBN : 82-575-0703-2

Lind O.C, Salbu B., Janssens K., Proost K., García-León M., García-Tenorio R. (2007). Characterization of U/Pu particles originating from the nuclear weapon accidents at Palomares, Spain, 1966 and Thule, Greenland, 168. *The Science of the Total Environment* 376, 294-305.

Lind, O.C.; Salbu, B.; Janssens, K. (2011). Microanalytical characterisation of radioactive TENORM particles, in: Barescut, J.C. (Ed.), International Conference on Radioecology & Environmental Radioactivity, Hamilton.

Lind O.C., De Nolf W., Janssens K., Salbu B. (2013) Micro-analytical characterization of radioactive heterogeinities in samples from Central Asian TENORM sites. *Journal of Environmental Radioactivity* 123, 63-70.

Pollanen, R., (1997) Highly Radioactive Ruthenium Particles Released from Chernobyl Accident: Particle Characteristics and Radiological Hazard. *Radiation Protection Dosimetry* 71, 23-32.

Popic, J., Meland, S., Salbu, B., Skipperud, L. (2014). Mobility of radionuclides and trace elements in soils from legacy NORM and undisturbed naturally ^{232}Th-rich sites. *Environmental Sciences: Processes and* Impacts 16, 1124-1134

Roos, P., (2008) Analysis of radionuclides using ICP-MS. In *Radioactivity in the Environment*, Elsevier pp 295-330

Salbu B. (2000) Source-related characteristics of radioactive particles. A review. *Radiation Protection Dosimetry* 92, 49-54.

Salbu, B., Janssens, K., Lind, O.C., Simionovici, A., Krekling, T., Drakopoulos, M., Snigireva, I., Snigirev, A. (2000). SR-based X-ray microbeam techniques utilised for solid state speciation of U in particles, in: T.Reich, D.Shuh (Eds.), Speciation, techniques and facilities for radioactive materials at synchrotron light sources - Workshop proceedings, Grenoble, France 10-12 September 2000, Grenoble, pp. 152-161.

Salbu, B., (2001) Actinides associated with particles. In Plutonium in Environment edited by A. Kudo, Elsevier, pp 121-138.

Salbu, B., Janssens, K., Krekling, T., Oughton D. (2001a) Micro-X-Ray Abnsorption Tomography and Micro-XANES for Charcaterization of Fuel Particles. *Nucl. Instrum. Meth. Phys. Research A* 467, 1249-1252

Salbu, B., Krekling, T., Lind, O.C., Oughton, D.H., Drakopoulos, M., Simionovici, A., Snigireva, I., Snigirev, A., Weitkamp, T., Adams, F., Janssens, K., Kashparov, V. (2001b). High energy X-ray microscopy for characterisation of fuel particles. *Nuclear Instruments and Methods A 467-468,1249-1252.*

Salbu B., Lind OC., Skipperud L. (2004) Radionuclide speciation and its relevance in environmental impact assessments. *Journal of Environmental Radioactivity* 74, 233-242.

Salbu B. (2016) Environmenta impact and risk assessments and key factors contributing to the overall uncertainties. *Journal of Environmental Radioactivity* 151, 352-360.

Salbu B. and Lind O.C. (2016). Radioactive Particlñes Released to the Environment from the Fukushima Reactors – Confirmation is still Needed. Integrated Environmental Assessment and Management 12, 687-689.

Skipperud, L. et al. (2016) Dispersion, Transfer and Risk of NORM and metals due to Construction in U-bearing Minerals. In Book of proceedings Second International Conference on Radioecological Concentration Processes- 50 years later, Seville, in press.

VIktorova, N.N., et al. (1993) Non-Destructive control of Chernobyl Hota Particles behavior and migration of radionuclides in soil-plant system. *Nucl. Tracks Radiat. Meas.* 22, 885-888,

Yamamoto, M., Tsukatani, T., Takayama, Y. (1996) Residual radioactivity in the soil of Semipalatinsk nuclear test site in the former Soviet Union. *Health Physics* 71, 142-148.

ANNEX

DATABASE

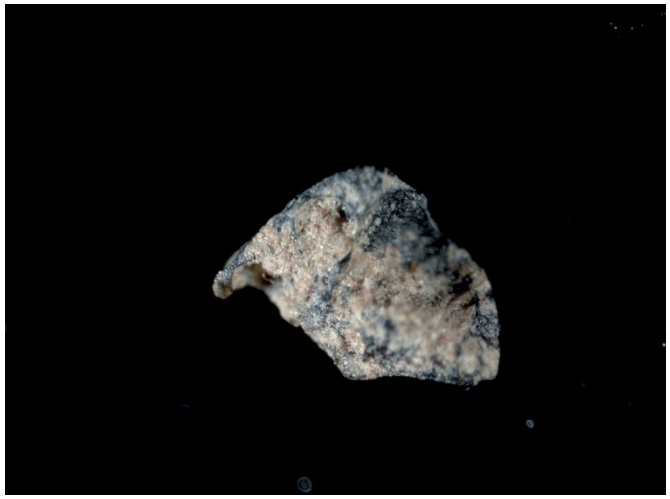
PARTICLES FROM NUCLEAR WEAPON TESTS

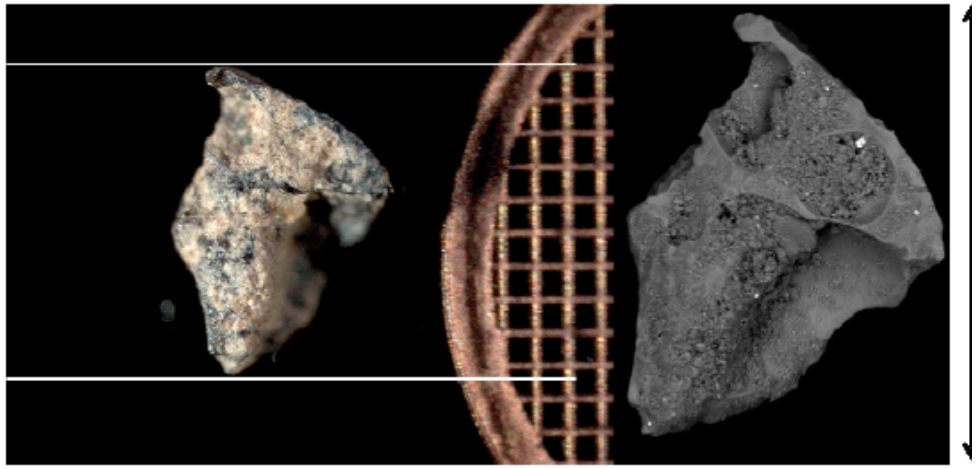
SEMIPALATINSK PARTICLE

CODE ID: TK 30 c

Photo from Optical microscope

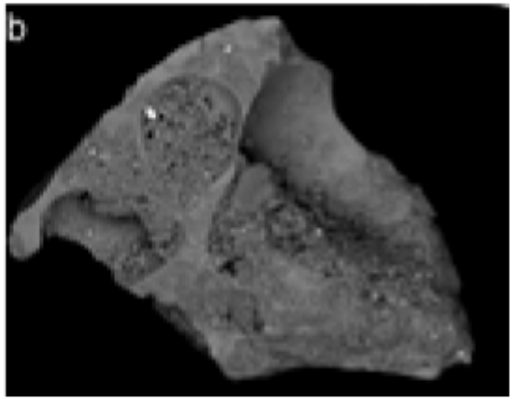
Maximum dimension of the particle: less than 1 mm





Particle isolated from a superficial soil collected at Tel´kem 2, excavation experiment performed in 1968 in the Semipalatinsk Nuclear Site (northeast Kazakhstan): This area was one of the main proving grounds for the testing of nuclear weapons by the former Soviet Union in the period 1949-1989.

SECONDARY ELECTRON IMAGE (SEM) of particle TK 30 c



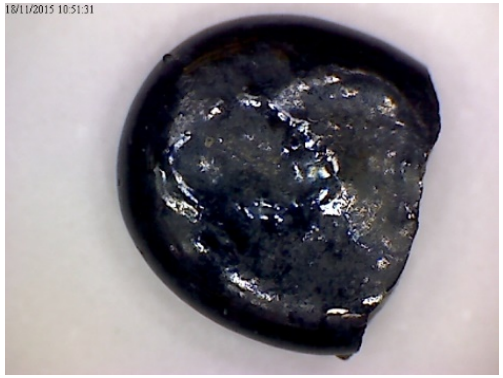
LOW-ENERGY GAMMA SPECTROMETRY of particle TK 30 c

Sample	^{239}Pu (Bq)	^{240}Pu (Bq)	^{241}Am (Bq)	^{152}Eu (mBq)	^{240}Pu/^{239}Pu (Activity)	$^{239+240}$Pu/^{241}Am (Activity)	^{240}Pu/^{239}Pu (Atoms)
TK30c	45± 5	6.6 ± 0.7	6.1 ± 0.2	34 ± 3	0.15 ± 0.03	8.5 ± 1.6	0.040 ± 0.007

In the particle the Pu is not the majority element as it can be deduced from its dimension and the total Pu activity determined.

The particle contains also some “long-lived” fission and neutron activation radionuclides such as ^{152}Eu and ^{60}Co, in agreement with their origin (nuclear weapon test).

SEMIPALATINSK PARTICLES
CODE ID: SPTK-1 AND SPTK-2



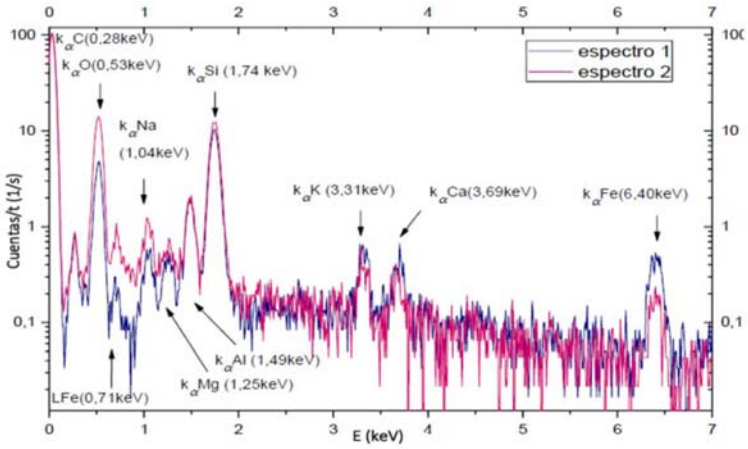


Photo SPTK-1 Optic Microscope *MICRO-PIXE ANALYSIS OF SPTK-1* *Photo SPTK-1 Optic Microscope*

Actinide content in the particles diluted due to their high dimensions (some mm).

Pu and U activity concentrations below the limit of detections by micro-PIXE and SEM-EDX.

GAMMA-RAY SPECTROMETRY

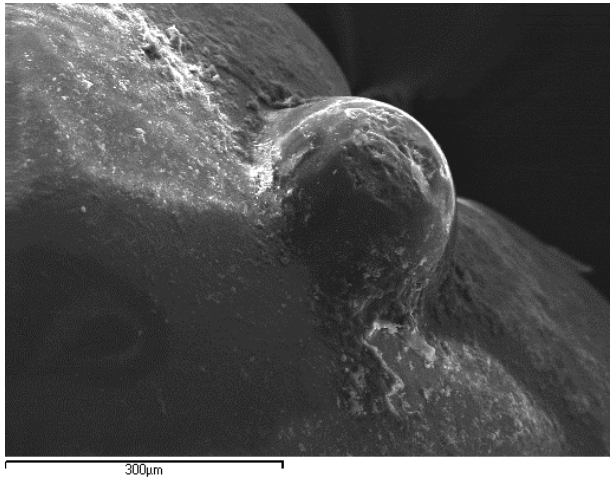
Partícle	Activity per particle (Bq)			
	^{241}Am	^{137}Cs	^{60}Co	^{152}Eu
SPTK1	20.2± 1.9	29.2 ±2.9	0.090± 0.017	7.21± 0.97
SPTK2	10.4± 0.9	23.2 ±2.1	0.025± 0.011	2.52 ±0.44

AMS DETERMINATIONS

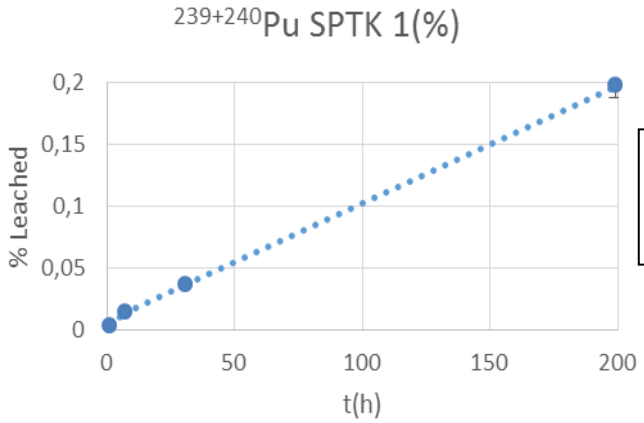
Particle	Atom ratios		
	$^{240}Pu/^{239}Pu$	$^{236}U/^{239}Pu$	$^{237}Np/^{239}Pu$
SPTK1	0.038±0.002	0.0039±0.0002	$1.3\ 10^{-4}\pm1.0\ 10^{-5}$
SPTK2	0.039±0.001	0.0044±0.0002	$1.4\ 10^{-4}\pm1.3\ 10^{-5}$

The particles have a glassy structure as can be deduced from the SEM images (secondary electrons)

Inert material with very low dissolution rate in HCl 0.16 M



SEM- IMAGE SPTK-1

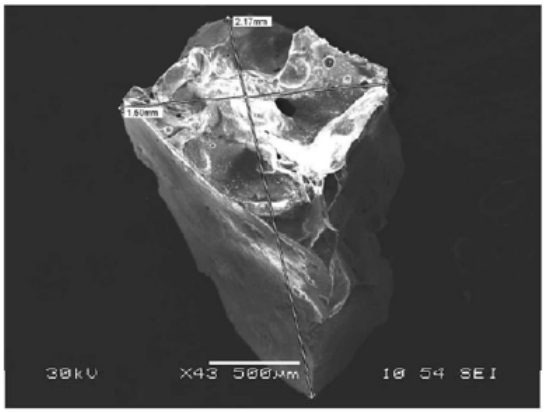


% of $^{239+240}$Pu leached from particle SPTK-1 as a function of time when was treated with HCL 0.16 M.

TRINITITE CONGLOMERATES
CODE ID: TRIN-1 and TRIN-2

Photo TRIN-1 obtained with an optical microscope

SEM IMAGE (Secondary Electrons) TRIN-2



The conglomerates are green-glassy minerals formed during the testing of the first US plutonium nuclear bomb (Trinity, 20 KT, New Mexico, USA, 1945)

The particles are formed by the fusion of products coming or generated in the bomb and soil. As in the particles of Semipalatinsk, the Pu in this particle is not a majority element. It contains also "long-lived" fission and neutron activation radionuclides.

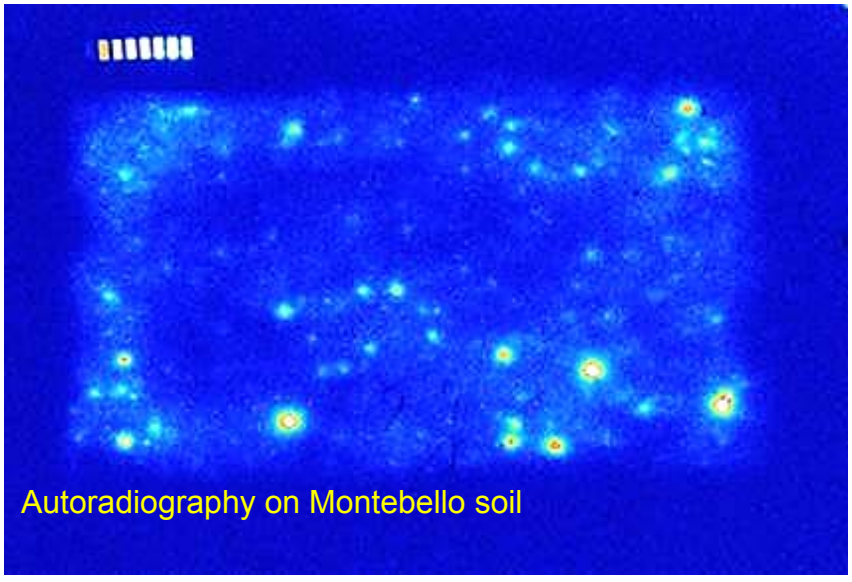
AMS DETERMINATIONS

Particle	Atom ratios		
	$^{240}Pu/^{239}Pu$	$^{236}U/^{239}Pu$	$^{237}Np/^{239}Pu$
TRIN-1	0.024±0.001	0.0014±0.0001	$1.5\ 10^{-4}$±$4.4\ 10^{-5}$
TRIN-2	0.026±0.001	0.0017±0.0001	$1.1\ 10^{-4}$±$3.4\ 10^{-5}$

PARTICLES FROM AUSTRALIAN WEAPON TEST SITES

List of particles available for Transformation studies

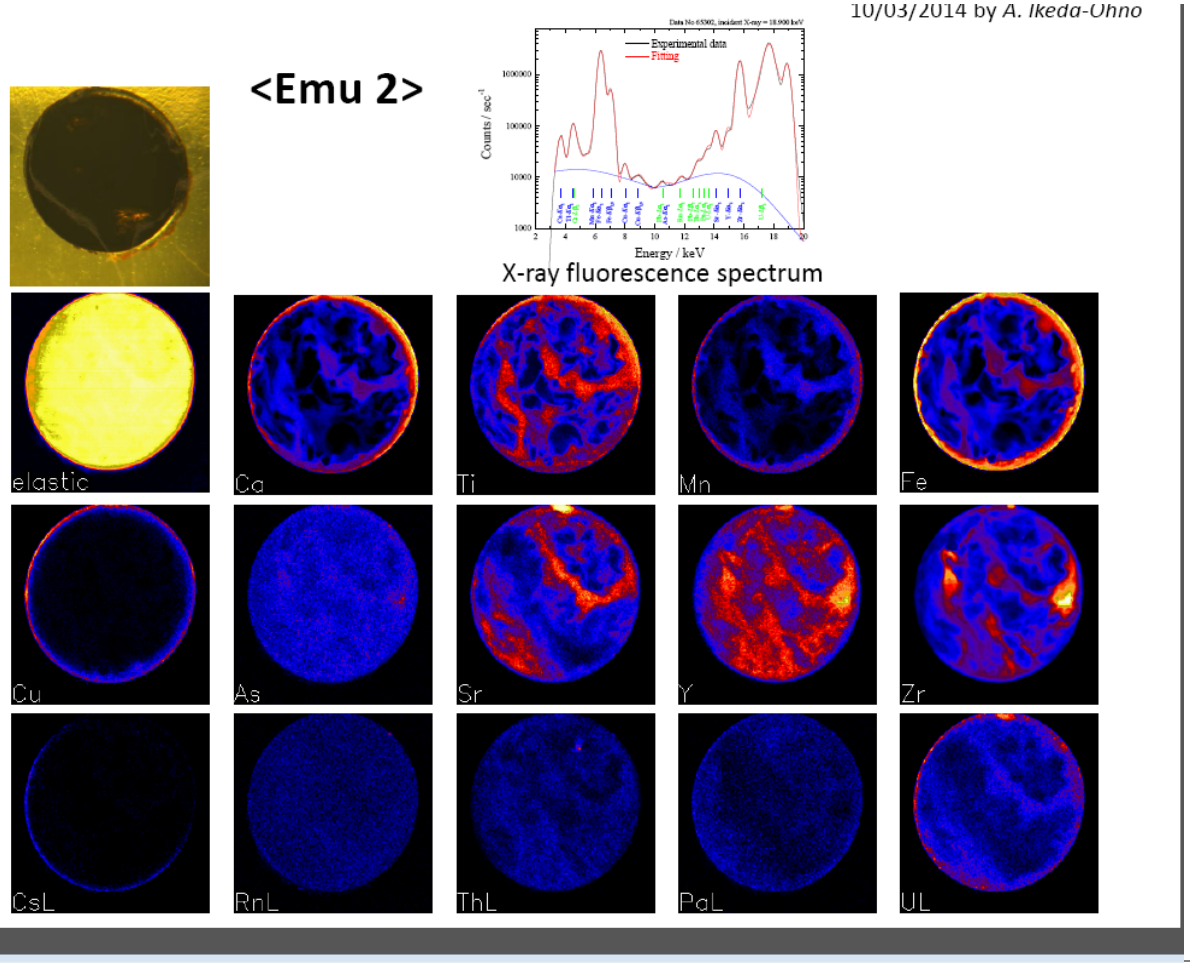
Location	Particle id.	Notes	Screening size (mm)	Screening activity (Bq)
Maralinga	One-Tree-2	Ellipsoid/oblong, glassy clear	0.6 x 0.8	5
Maralinga	BreakAway-2	Ellipsoid, clear	0.3 x 0.6	2
Maralinga	Marcoo-3	Sphere, clear, dark brown/black colour	0.5	5
Emu	Totem II -3	Sphere, glassy, opaque black	0.4	3
Monte Bello	Hurricane-Trimouille-3	Oblong/triangle, white-brown	0.4	1
Monte Bello	G2-shallowseds-1	White-brown grain	0.5	0.5
Monte Bello	G2 soil-1	Conglomerate, dark centre with glassy surface and adhered grains	0.5 x 1.0	4



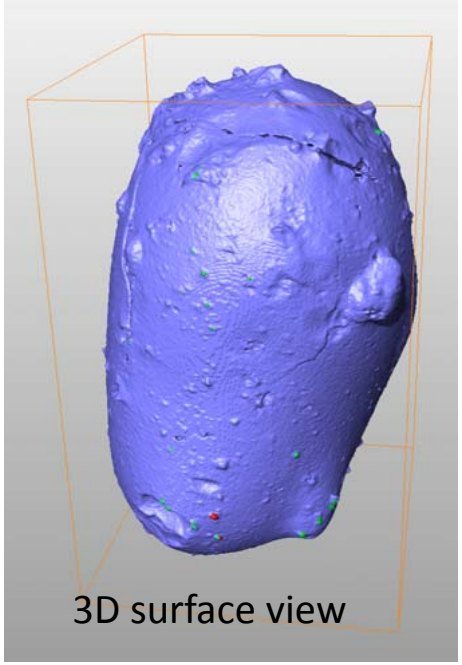
Autoradiography of a soil sample collected at Monte Bello test site, showing the high density of radioactive particles with different sizes and radioactive content.

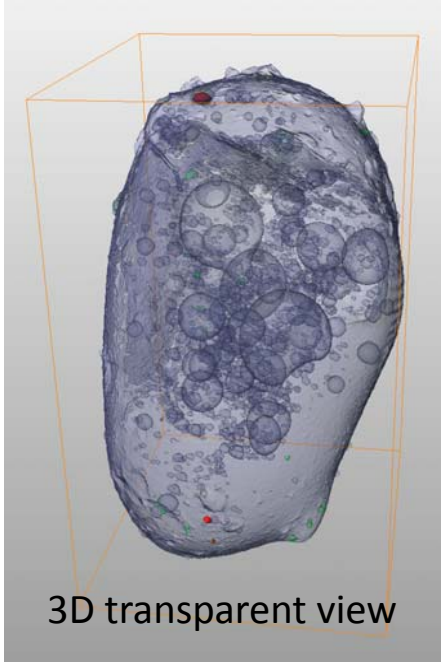
Fission test particle, Emu, Australia CODE ID: Emu-2

One of numerous post fission test particles from the Totem II, Emu site, Australia. This particle was spherical before being sanded to form a half-sphere shape. It was analysed on with the flat surface facing the XFM beam.



μ-SR-XRF





Density index

Fission test particle, Maralinga, Australia

Particle One-Tree-2

Nano-CT image

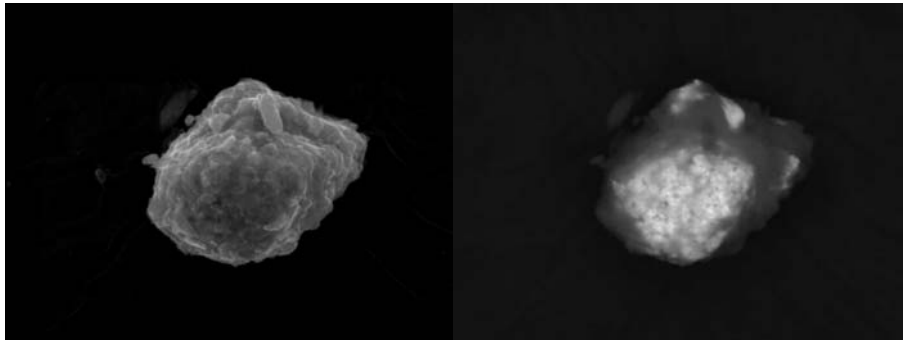
Glassy structure with some inclusions of high-density containing the actinide contents. Some of the inclusions are on the surface of the particle, others inside the particle. Location of the inclusions relevant for the leaching experiments.

Inclusions Characteristics

Particle ID	Volume-equivalent sphere diameter [µm]	Surface-equivalent sphere diameter [µm]	Surface [µm^2]	Volume [µm^3]	Sphericity	Mean density index	Max density index
1	13	14	640	1140	0.83	251	255
2	5	5	88	66	0.90	251	255
3	2	2	19	6	0.85	246	255

Particles from Conventional Detonations of Nuclear Weapons: Palomares

PALOMARES PARTICLE number 1 CODE ID: A3 (ZONE 2)

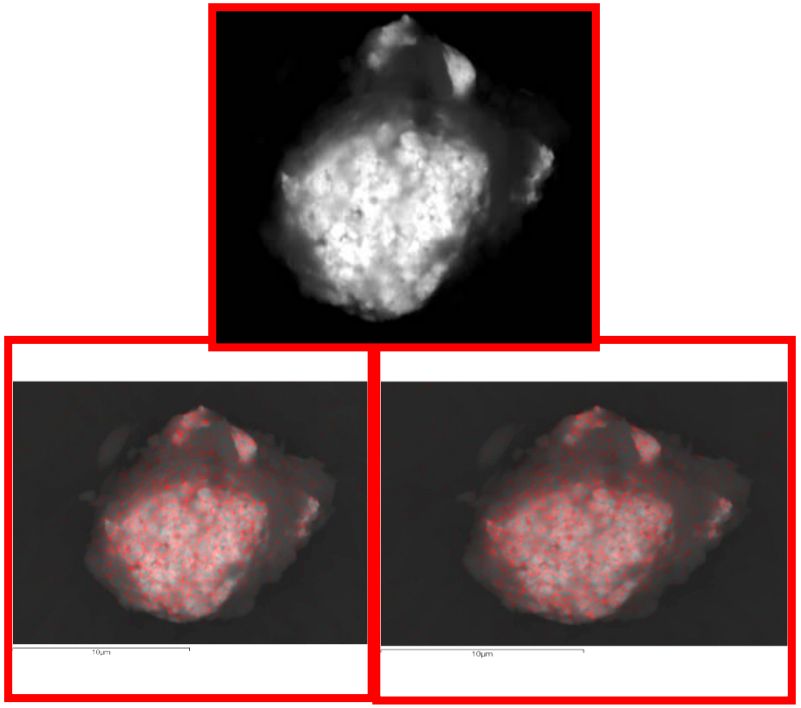


Pu/U e^-	Pu/U He^{2+}	Pu/U H^+
1.19	1.24	1.23
1.18	1.28	1.28
1.27	1.25	1.20
1.19		
1.30		
1.34		
Average 1.25	Average 1.26	Average 1.24

Atom ratios of Pu/U in the particle A3 obtained through electrons of 30 keV (SEM-EDX) and with protons of 3 MeV and alpha-particles of 5.45 MeV (μ-PIXE). The results indicate a uniformity of the Pu/U atom ratio along the depth of the particle.

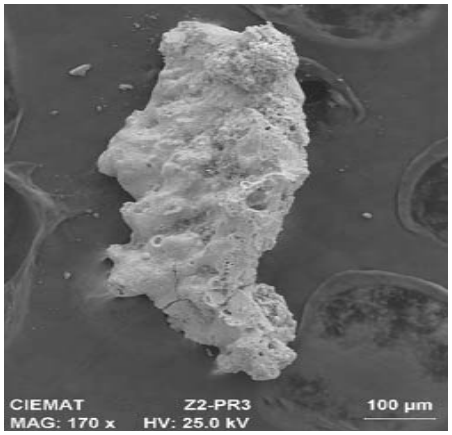
GAMMA-RAY SPECTROMETRY, particle A3

Sample	^{239}Pu (Bq)	^{240}Pu (Bq)	^{241}Am (Bq)	^{240}Pu/^{239}Pu (Activity)	$^{239+240}$Pu/^{241}Am (Activity)	^{240}Pu/^{239}Pu (Atoms)
A3	27 ± 3	5.7 ± 0.9	5.2 ± 0.2	0.22 ± 0.05	6.3 ± 1.5	0.059 ± 0.013



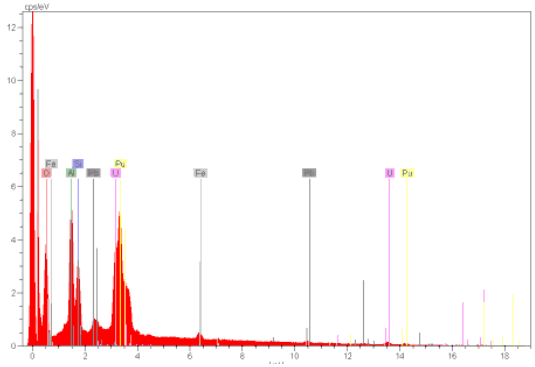
X-ray mapping of Pu (left) and U (right) performed by SEM-EDX in particle A3

PALOMARES PARTICLE number 2
CODE ID: Z2-PR3



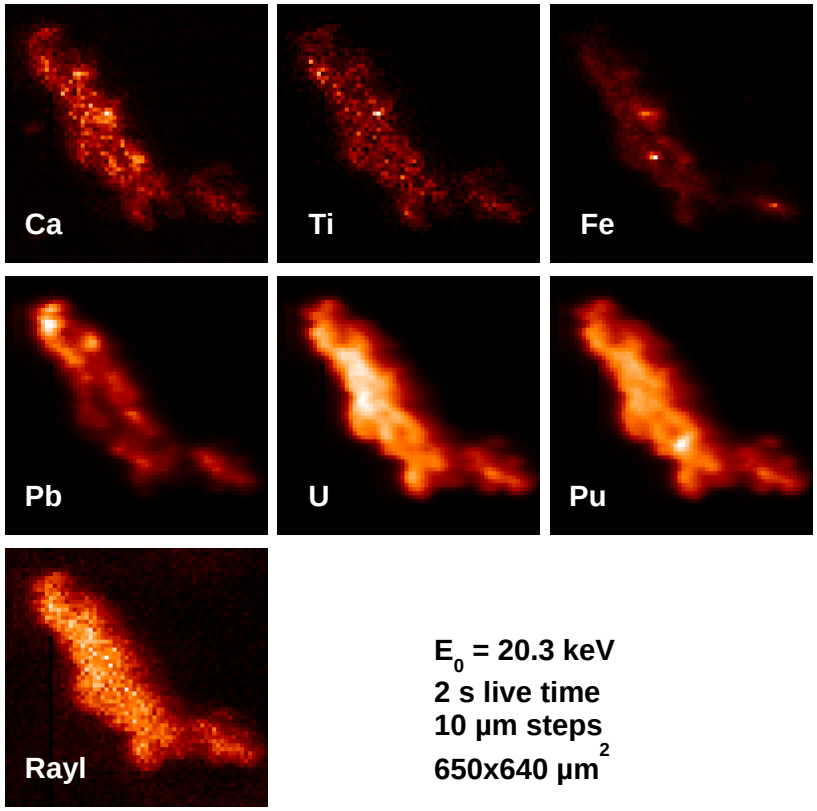
The particle has an elongated shape, being the largest dimension of approximately 500 µm. It is a porous material with granular texture and with the existence of fractures.

SEM-EDX ANALYSIS of particle Z2-PR3



By SEM-EDX analyses (x-ray microanalysis) it has been confirmed the presence in the particle Z2-PR3 of Pu and U in a mass proportion 55:45.

μ-XRF of particle Z2-PR3 at HASYLAB

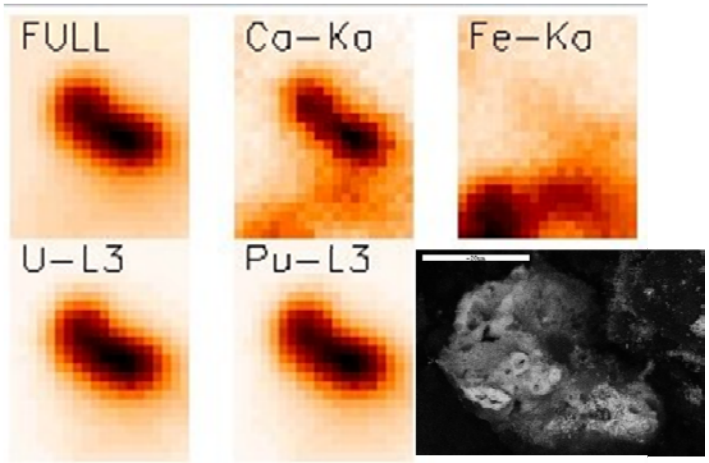


E_0 = 20.3 keV
2 s live time
10 μm steps
650x640 μm^2

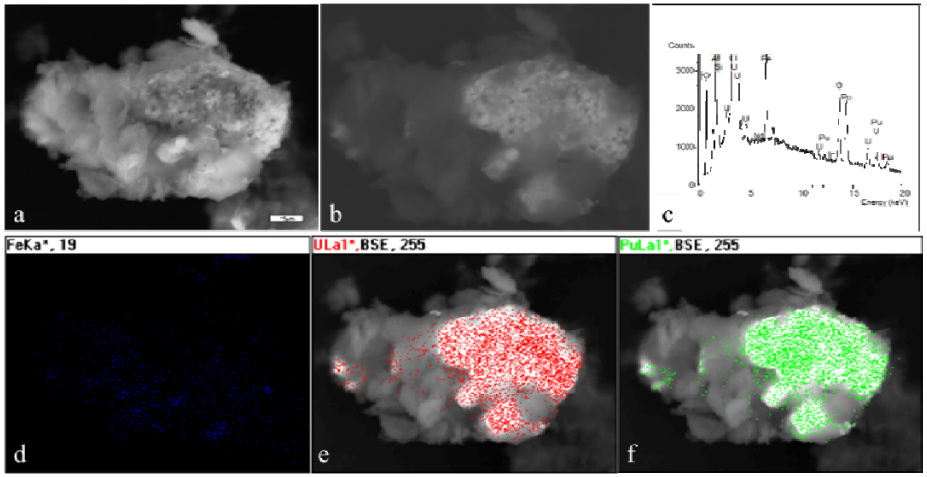
μ-XRF analyses performed in the particle with synchrotron radiation indicates that the distribution of Pu and U in the particle is quite homogenous, being both elements the majority ones.

Palomares Particles 3 and 4

Particle	Size (μm)	^{241}Am (Bq)
Ham 128	45	6.2
Ham 130a	50	13.5



μ-SRXRF mapping of Ca, Fe, U and Pu as well BEI mode image of particle Ham 130a



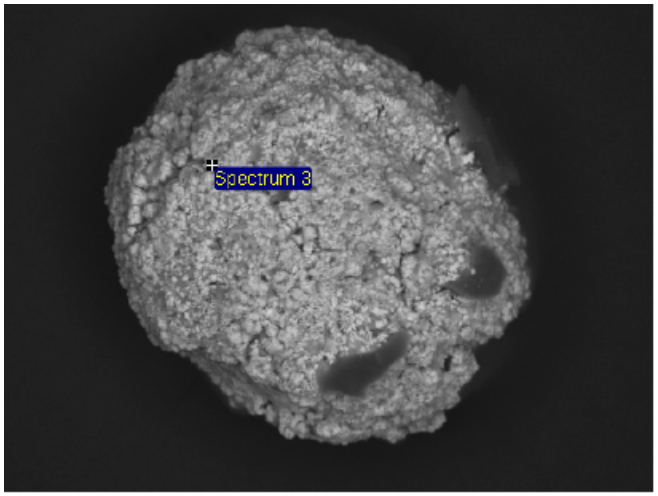
Scanning electron microscopy of particle Ham 128 isolated from soils collected at Palomares, Spain: (a) Secondary Electron Imaging (SEI) mode reflecting the morphological structure of the particle, (b) Backscattered Electron Imaging (BEI) mode showing the distribution of high atomic number elements, (c) elemental spot analysis by XRMA, (c) and (d-f) X-ray mapping of Fe, U and Pu superimposed on a BEI mode image. Bar 5 μm.

PALOMARES PARTICLE number 5
CODE ID: PC-15

Actinide determination by X-ray spectrometry using LEGe detector, particle PC-15 (CIEMAT)

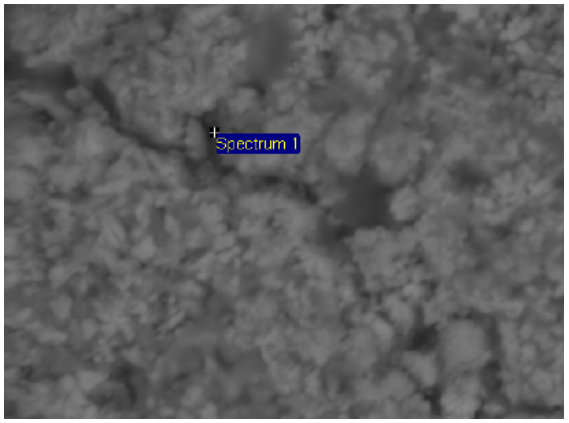
Sample	^{241}Am (Bq)	$^{239+240}$Pu/^{241}Am (Activity)
PC-15	400 ± 8	4.3 ± 0.2

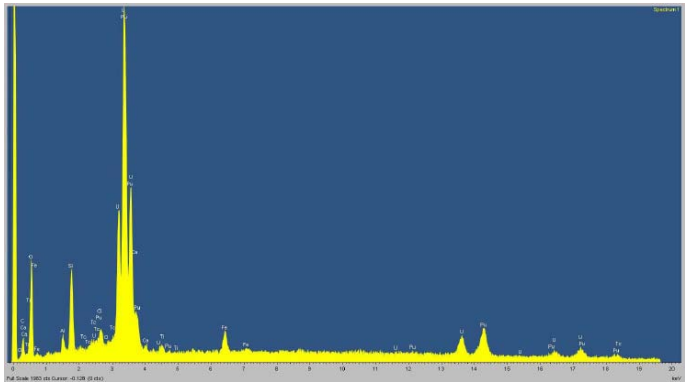
SEM-EDX ANALYSIS, particle PC-15



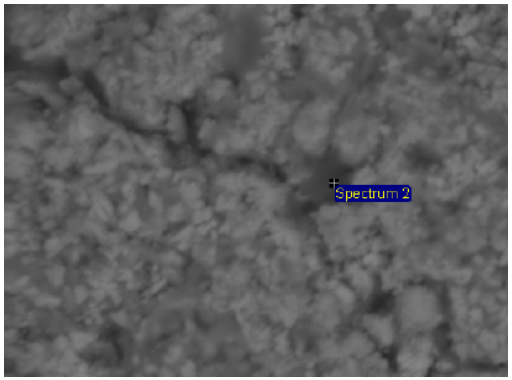
Spherical particle with a diameter of about 50 μm, and with a granular structure in the surface (US).

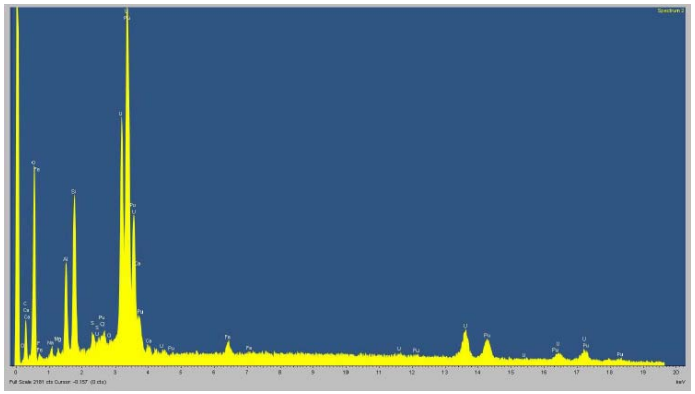
SEM-EDX ANALYSIS, particle PC-15





At the point of analysis the Pu peak is slightly higher than the U peak.





In another point of the surface we found the opposite: The U peak is slightly higher than the Pu peak.

The SEM-EDX analysis performed at different points of the particle PC-15 shows that the distribution of Pu and U in the particle is non homogeneous, with some oscillations in the atomic Pu/ U ratio.

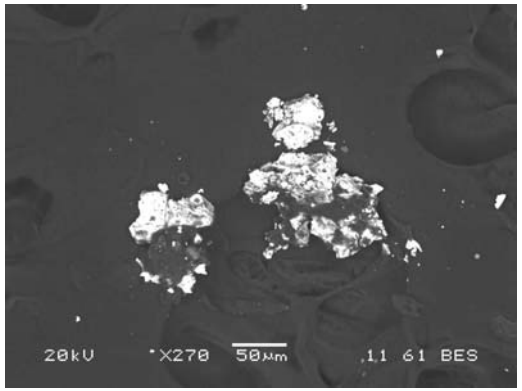
PALOMARES PARTICLE number 6
CODE ID: P-134/D

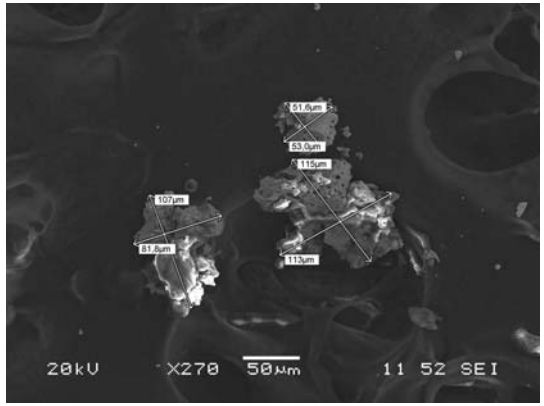
Actinide determination in P-134/D by X-ray spectrometry using LEGe detector (CIEMAT)

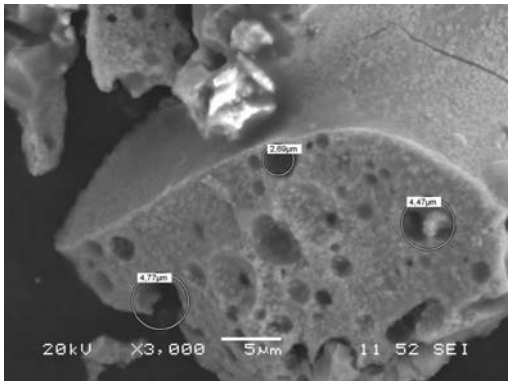
Sample	^{241}Am (Bq)	$^{239+240}$Pu/^{241}Am (Activity)
P-134-D	219 ± 4	4.3 ± 0.2

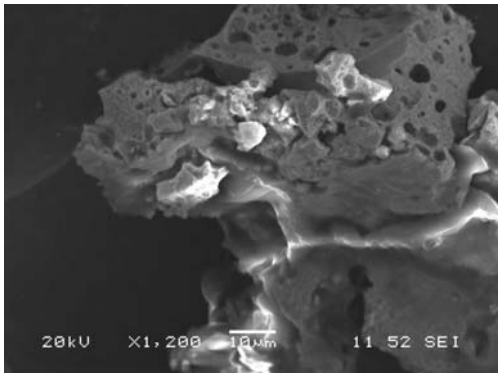
SEM-EDX ANALYSIS, particle P-134/D

Very fragile particle. In fact it experimented its fractionation in various pieces when was mounted on the planchet to perform the SEM-EDX analyses (CIEMAT,US).





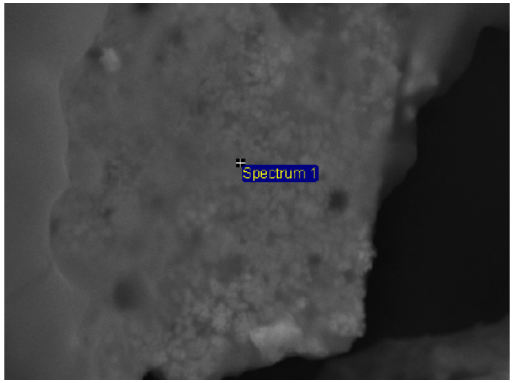


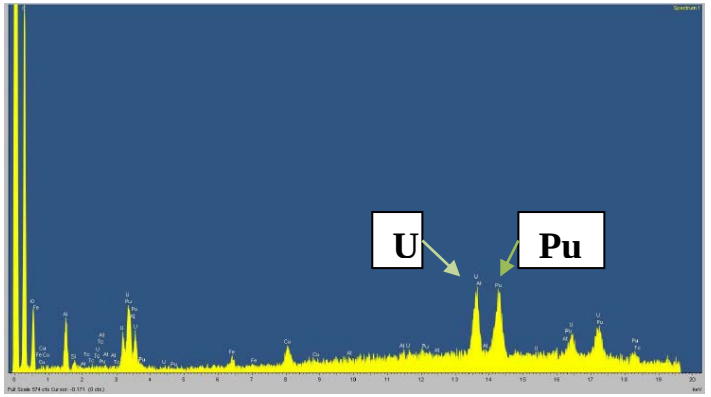


High resolution images of particle P-134/D obtained with secondary electrons, show how porous is the particle under analysis and give additional evidences about its fragility.

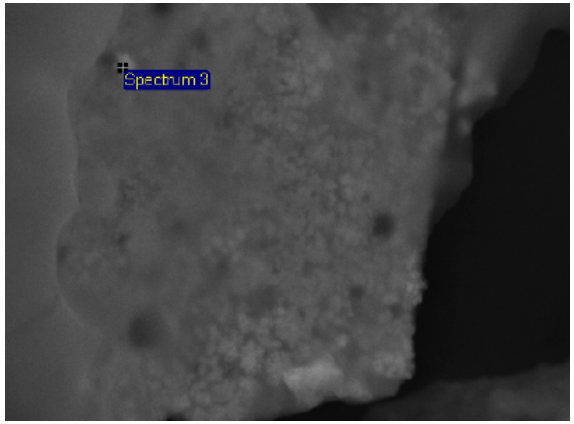
EDX analysis, particle P-134/D

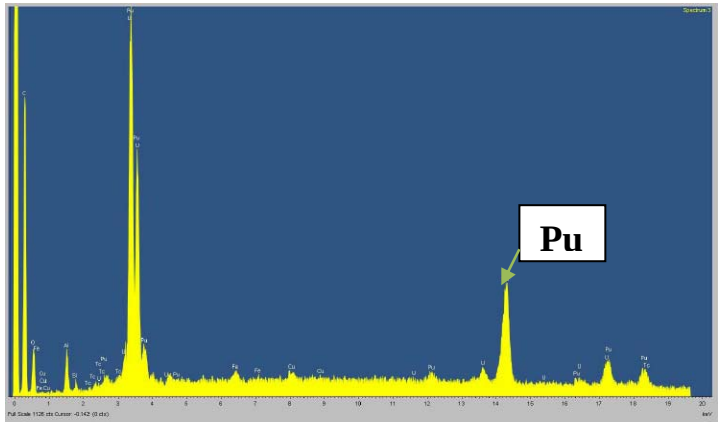
The EDX analysis performed at different points of the particle P-134/D shows that the distribution of Pu and U in the particle is non homogeneous, with very clear oscillations in the Pu/ U ratio.



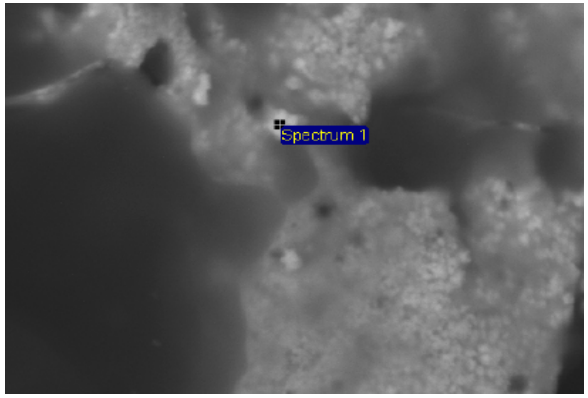


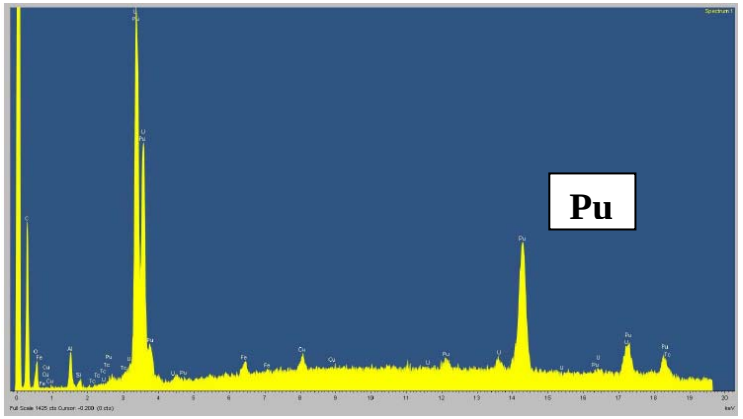
The analysis in a point of the surface shows a Pu/U peak ratio near to 1





The analysis of a grain in the surface indicates that is mainly formed by Pu, with only traces of U.

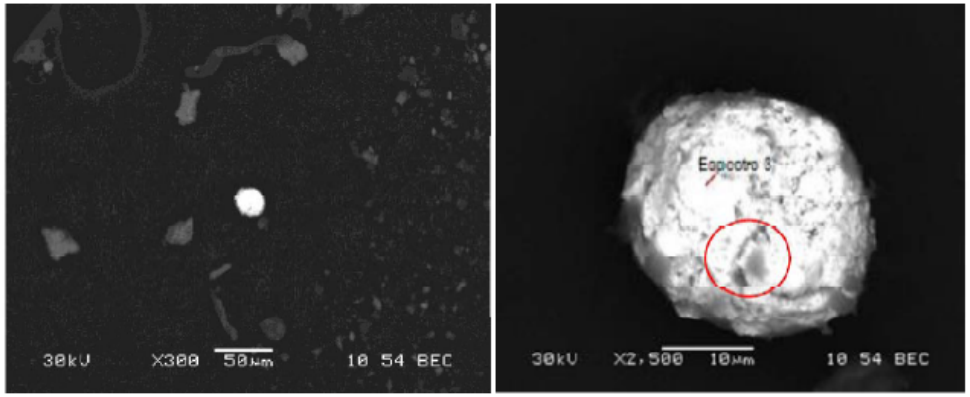




Inside a general uniform distribution of U and Pu in the particle, it is possible to find embedded in the sample some "grains" formed mainly by Pu.

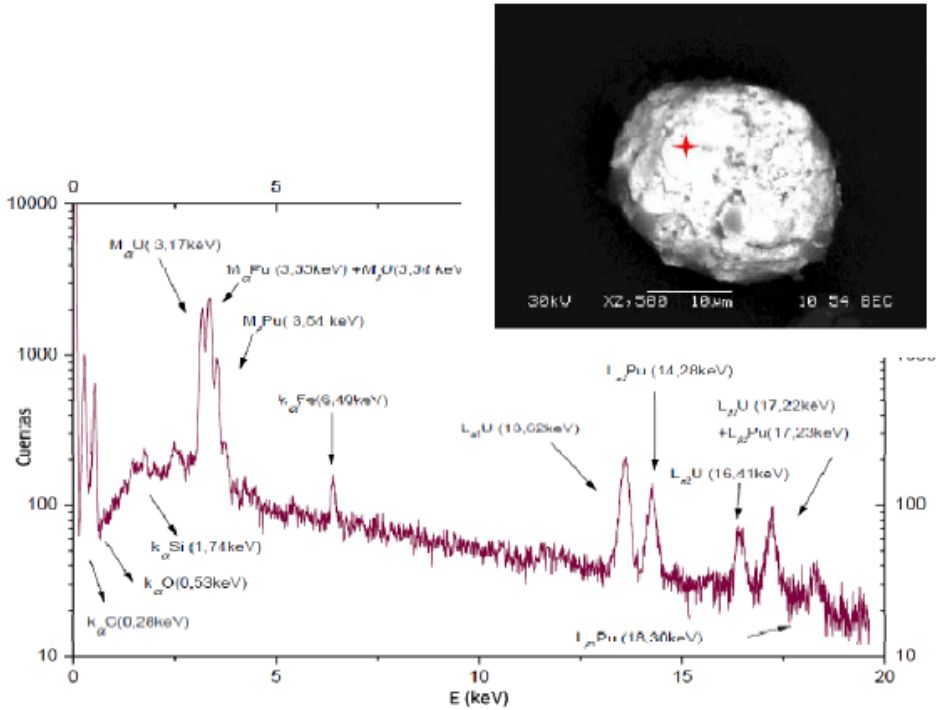
PALOMARES PARTICLE number 7
CODE ID: EC-1

SEM IMAGE (BACK-SCATTERING MODE)



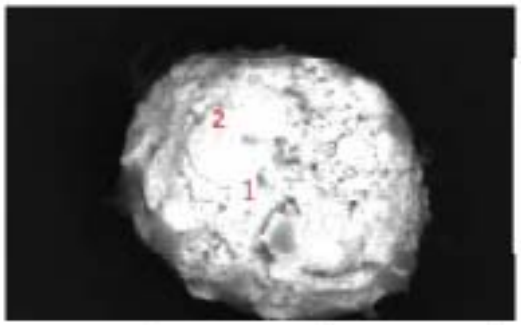
GAMMA-RAY SPECTROMETRY

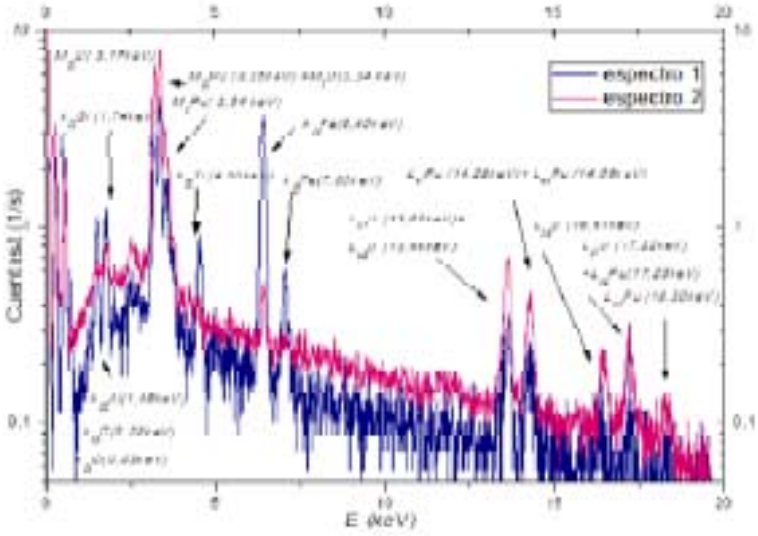
^{241}Am (Bq)	8,6 ± 0.3

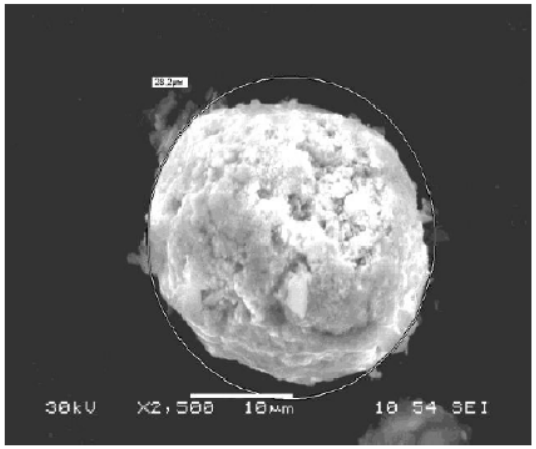


X- RAY SPECTRA PUNCTUAL ANALYSIS SEM-EDX

X-RAY SPECTRA BY μ-PIXE

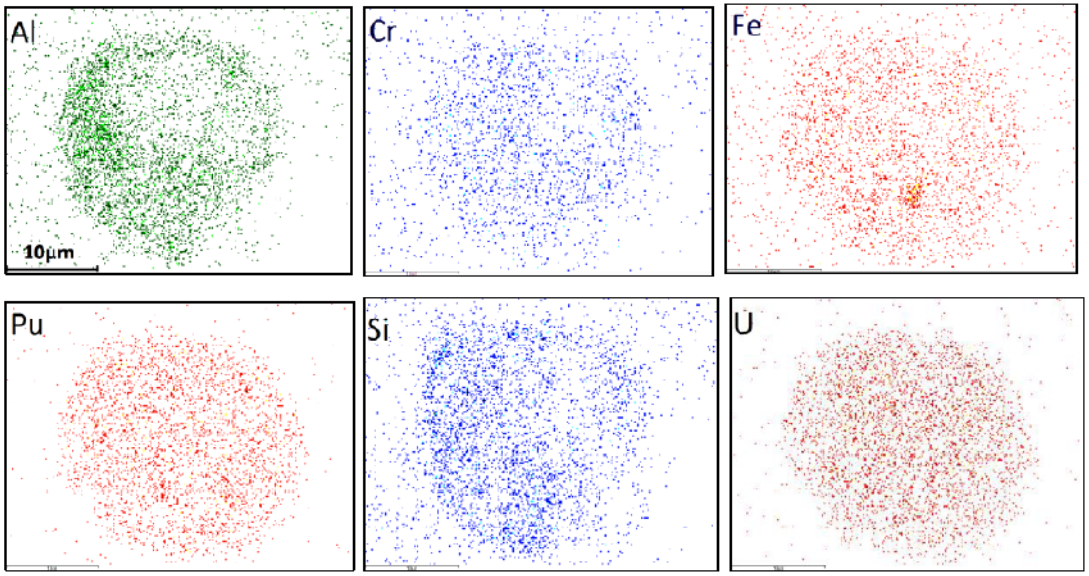






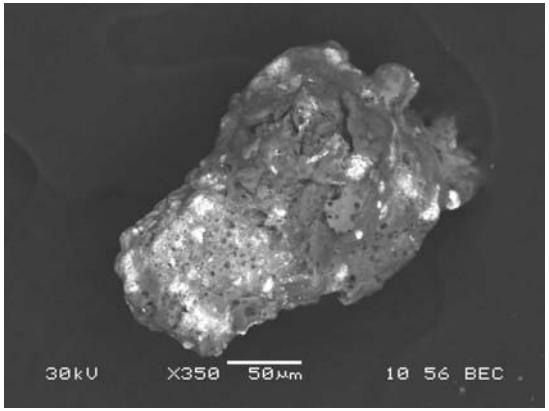
SEM IMAGE

(SECONDARY ELECTRON MODE)

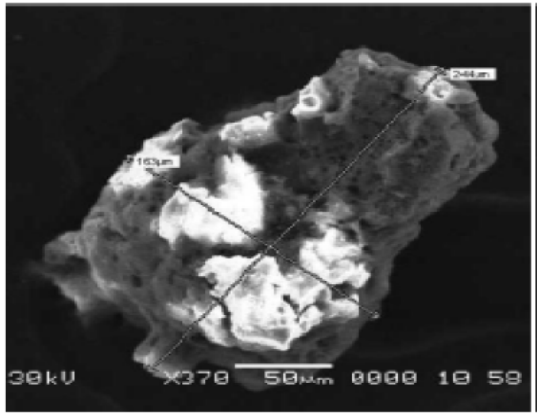


X-RAY MAPPING BY μ-PIXE

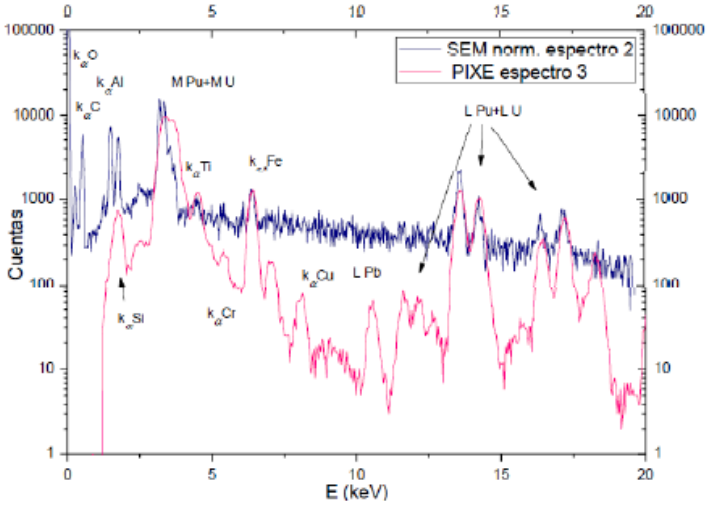
PALOMARES PARTICLE number 8
CODE ID: 2058-125-D



SEM (BEI)

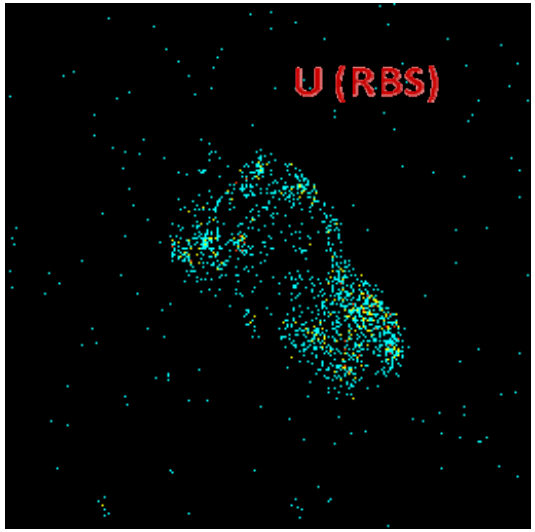


SEM (SE)

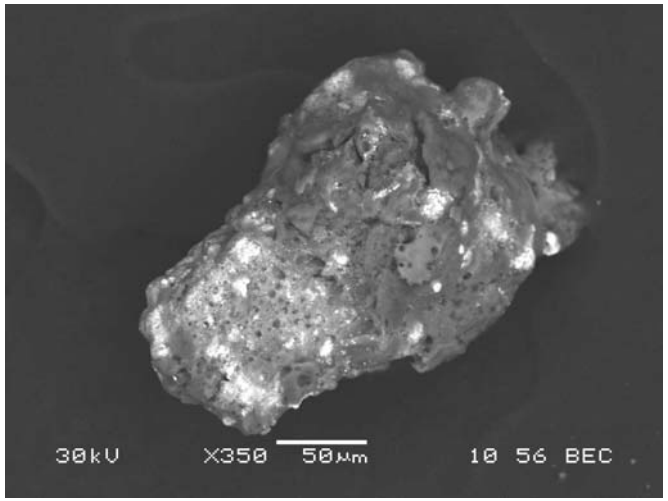


X-RAY SPECTRA SEM-EDX/µ- PIXE

PU/U elemental ratio	
µ-PIXE	SEM
0.80	0.36
0.90	0.25
0.79	0.39
0.51	0.43
	0.25
	0.51

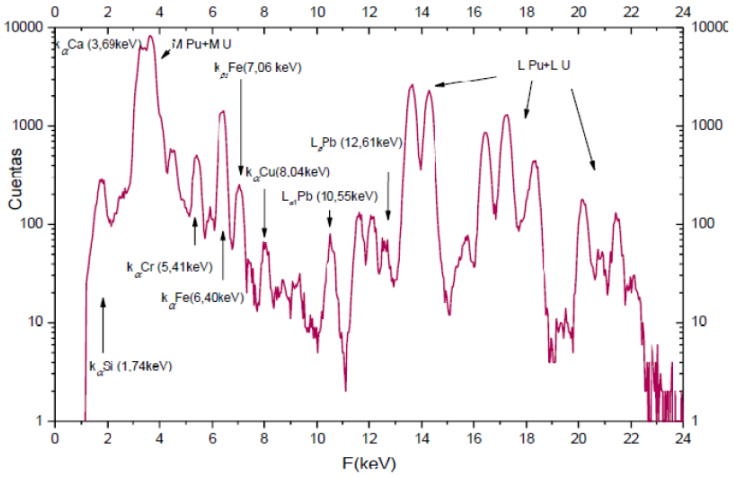


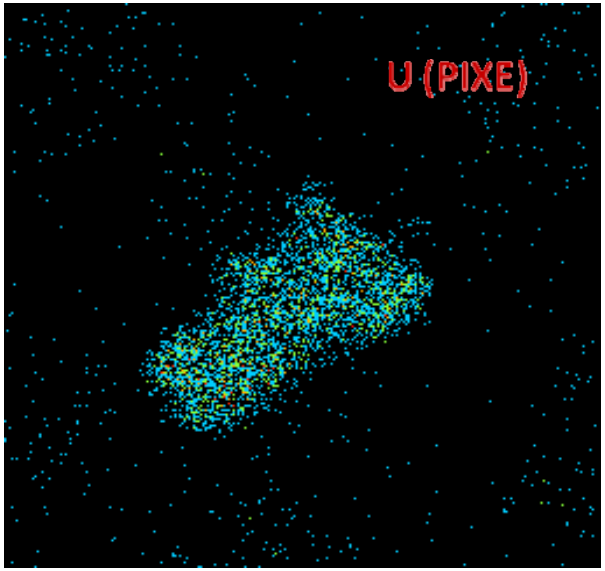
Scan: 500*500 um²

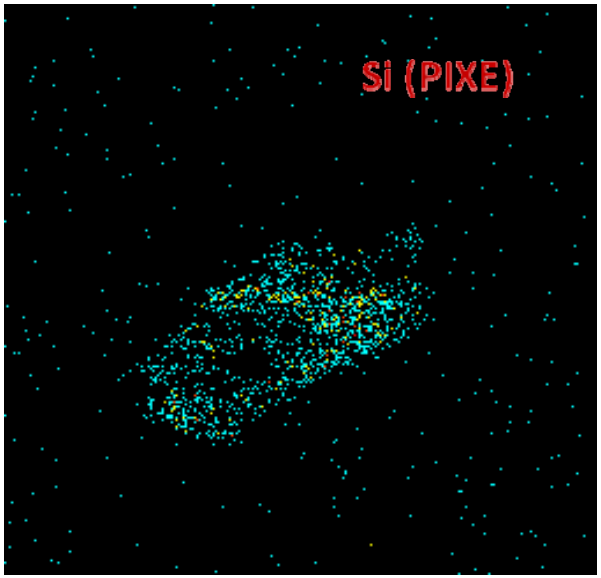


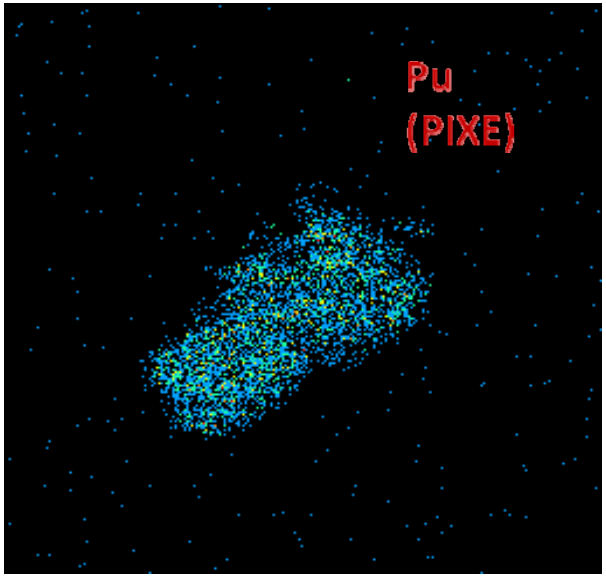
µ-PIXE

INFORMATION



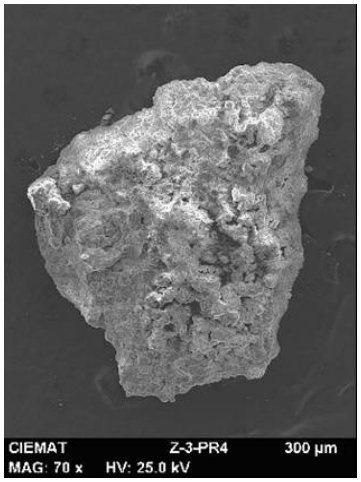






Scan: 500*500 um²

PALOMARES PARTICLE number 9
CODE ID: Z3 PR4 (ZONE 3)



The particle Z3 PR4 has a parallelogram shape, being its largest dimension 1400 µm. It has a granular texture, being confirmed by SEM-EDX the presence of Pu and U in a mass proportion of 84: 16

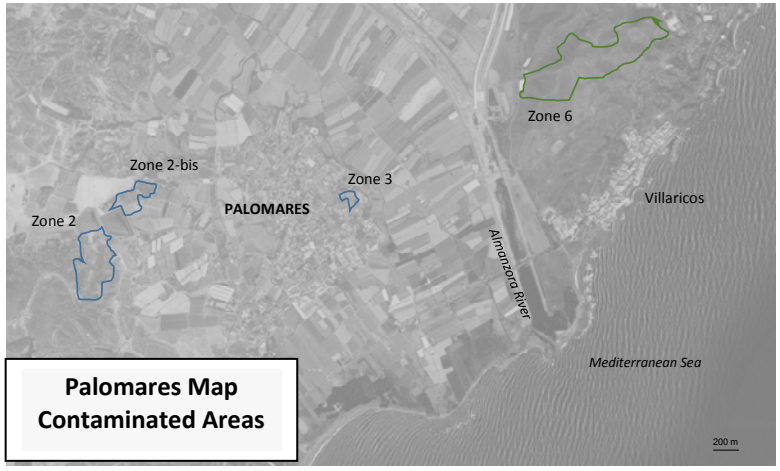
S E M – E D X, particle Z3 PR4

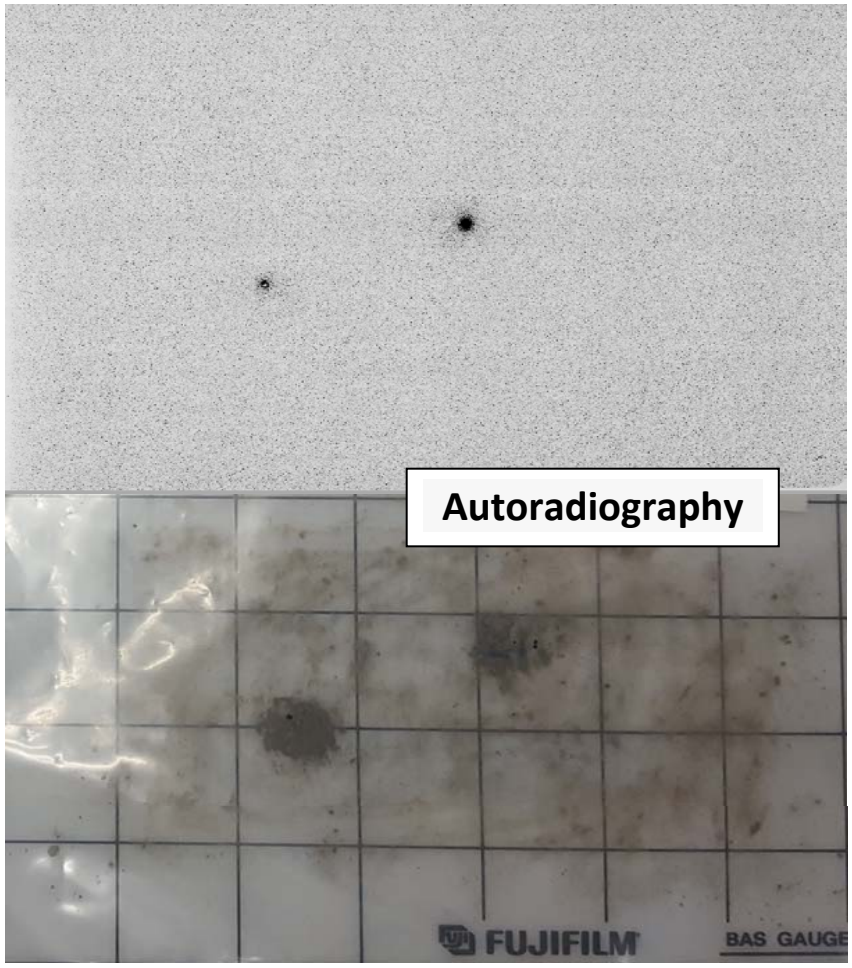
Reference	Oxygen	Aluminium	Calcium,%	Lead,%	Uranium,%	Plutonium,%	Others (Fe, Cu, Zn, Ti) %
Z-3 PR-4			37 ± 25	16 ±11	5 ± 3	28 ±12	<5

LOW ENERGY GAMMA SPECTROMETRY, particle Z3 PR4

Sample	^{239}Pu (Bq)	^{240}Pu (Bq)	^{241}Am (Bq)	^{240}Pu/^{239}Pu (Activity)	$^{239+240}$Pu/^{241}Am (Activity)	^{240}Pu/^{239}Pu (Átoms)
Z3PR4	2210± 160	383±37	594±18	0.17 ± 0.03	4.5 ± 0.7	0.048 ± 0.007

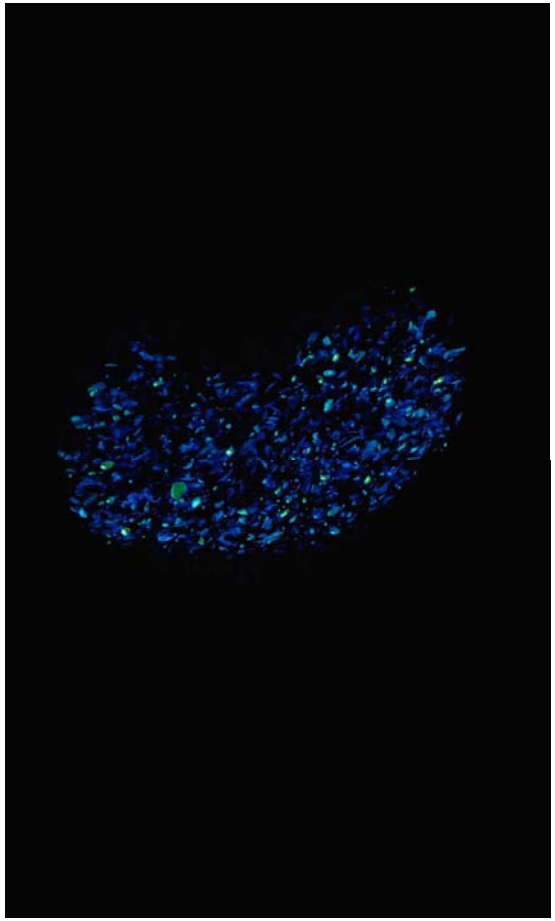
PALOMARES PARTICLE number 10
CODE ID: S6 (zone 6)



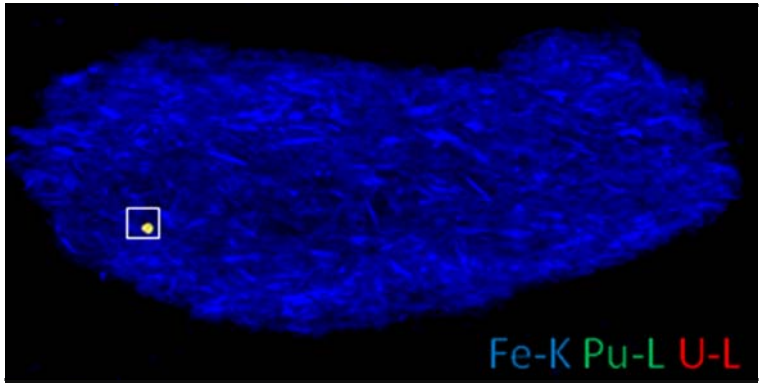


Nano-CT/submicron-XRF characterization

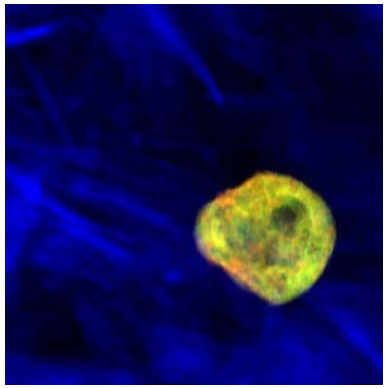
Inclusion in sediment grain



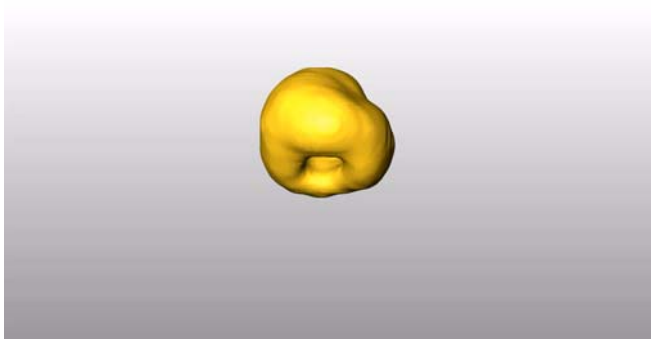
Nano-CT
of sediment grain



μ-XRF (1,5 x 1,5 μm² step size, 314 x 258 μm² scan size)



Submicron-XRF
(0,25 x 0,25 μm² step size
69,276 x 69,25 μm² scan size)

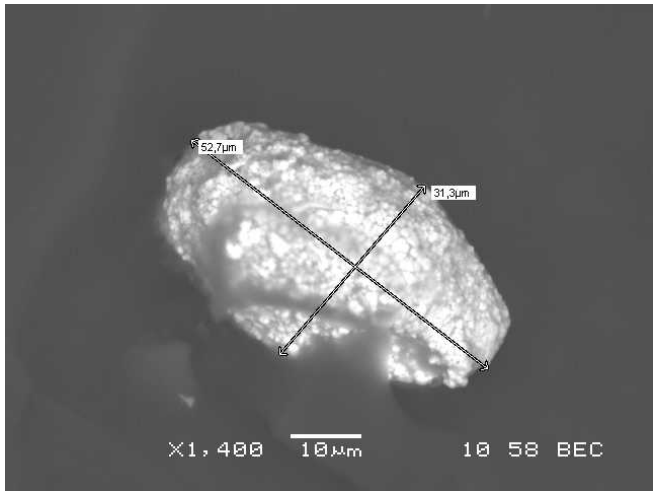


3D view surface

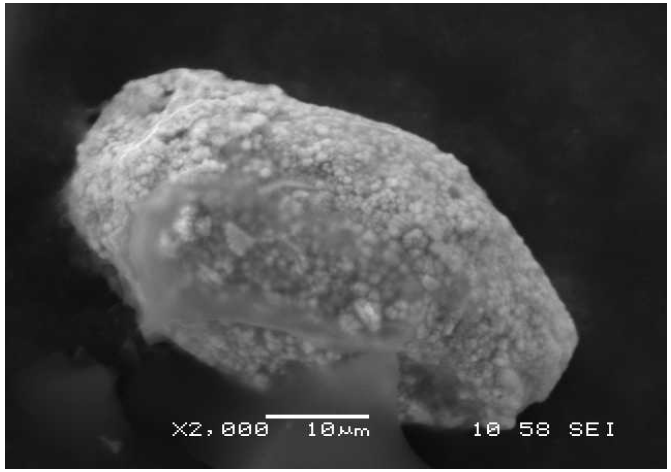
Particles from Conventional Detonations of Nuclear Weapons: Thule

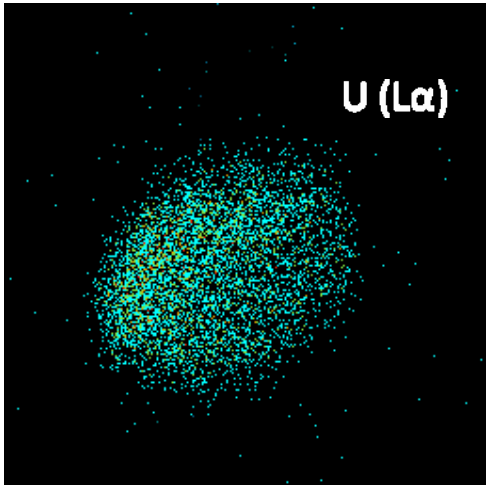
CODE: THULE-2 (TERRESTRIAL AREA)

PARTICLE 1



GAMMA-RAY SPECTROMETRY	
^{241}Am (Bq)	10 ± 2

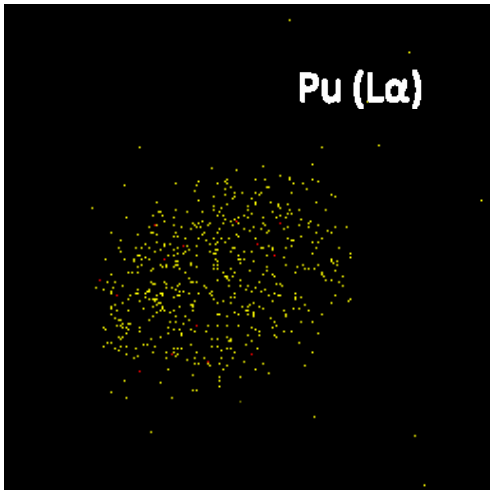


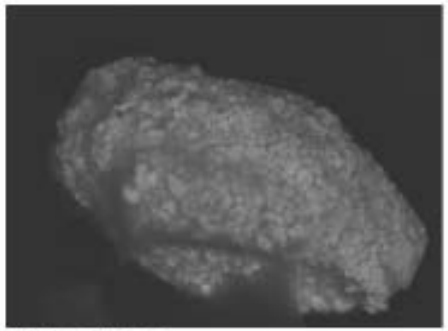


SEM IMAGES (up)

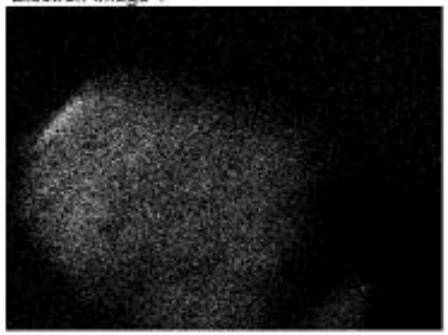
AND

μ-PIXE MAPPING (down)

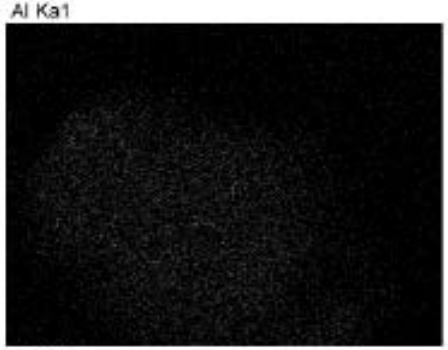




Electron Image 1



Al Ka1

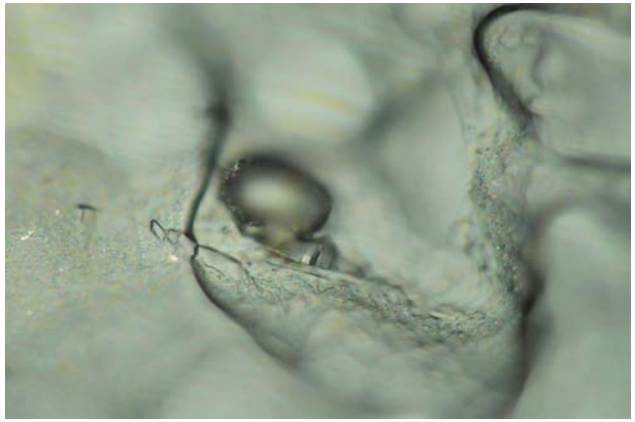


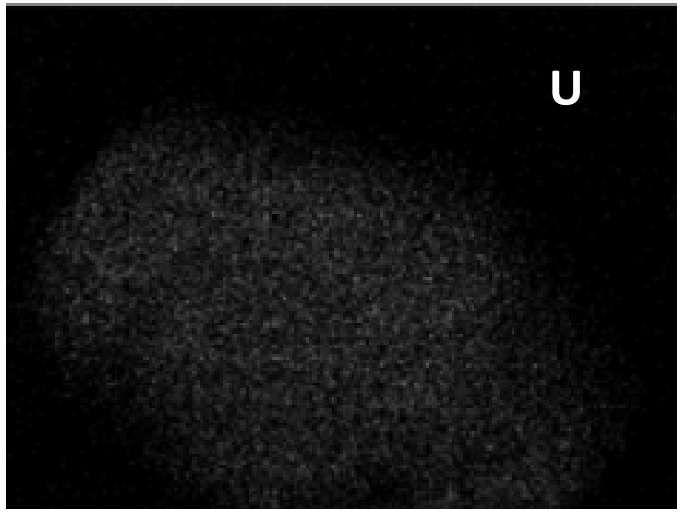
Fe Ka1

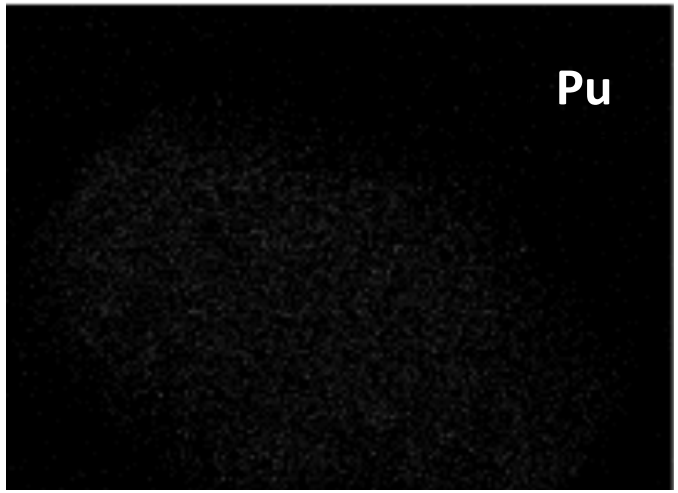
MAPPING SEM-EDX

AND

OPTIC MICROSCOPE IMAGE



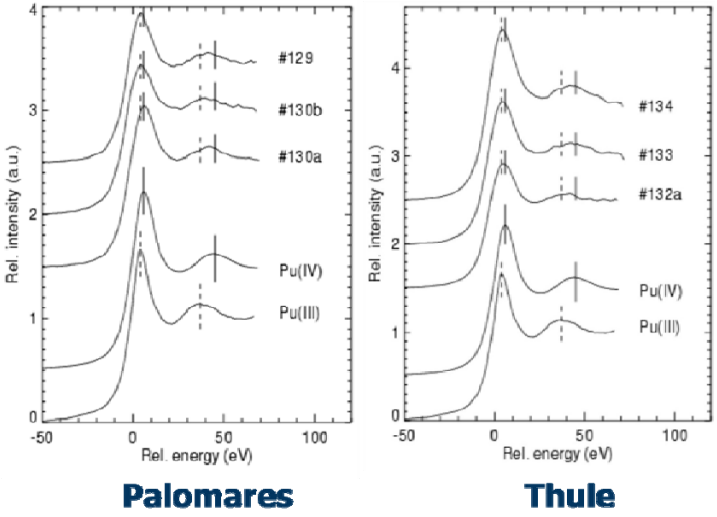




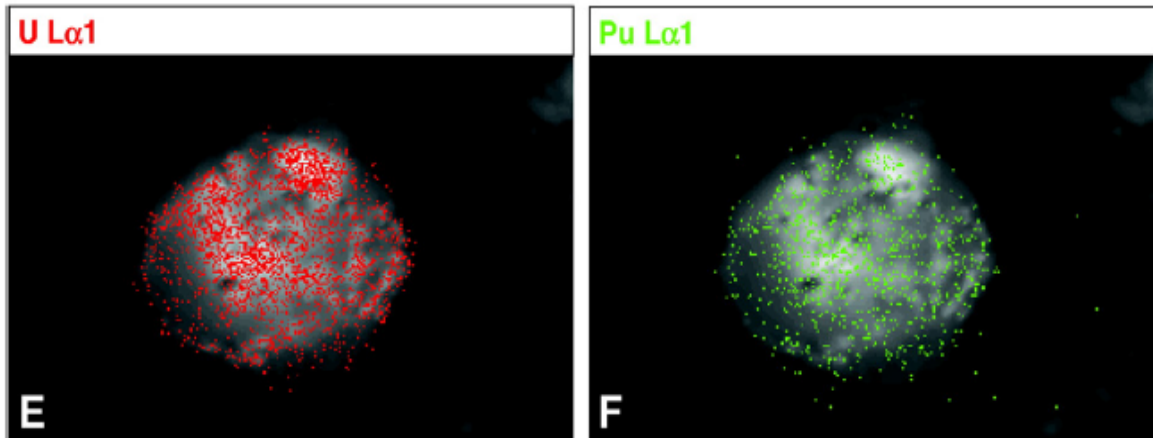
THULE PARTICLES 2 AND 3 (marine origin)

CODES: HAM-133 y HAM-134

Particle	Size (μm)	^{241}Am (Bq)
Ham 133	40	1.2
Ham 134	20	2.8



Fluorescent Pu μ-XANES profiles obtained from different Palomares and Thule particles, including some of the available ones for the transformation studies ***(Lind et al., 2007)***.

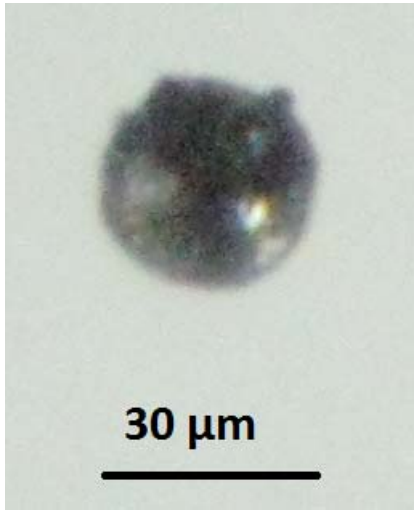


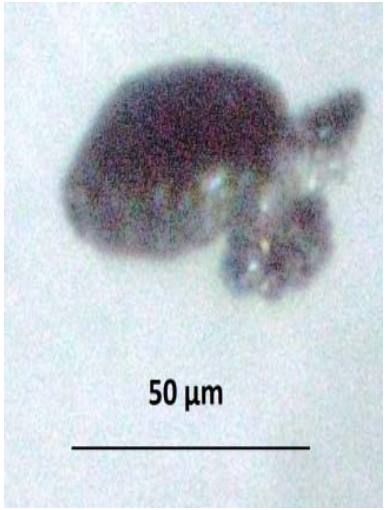
Scanning Electron Microscopy (SEM) and Energy Dispersive X-ray analysis of the particle Ham 134 isolated from Thule sediment. Left image: X-ray mapping of U superimposed on an image recorded in Backscattered Electron Imaging (BEI) mode image. Right image: X-ray mapping of Pu superimposed on an image recorded in Backscattered Electron Imaging (BEI) mode image.

THULE PARTICLES 4 a 9
CODE IDs: PC-1, PC-2, PC-4, PC-5, PC-6 and PC-7

A total of six hot-particles were isolated by DTU and are available for the transformation studies. The dimensions of these particles oscillate between 25 and 60 μm.
In general are quite fragile, suffering quite easily their fragmentation.

IMAGES OBTANIED BY OPTIC MICROSCOPE



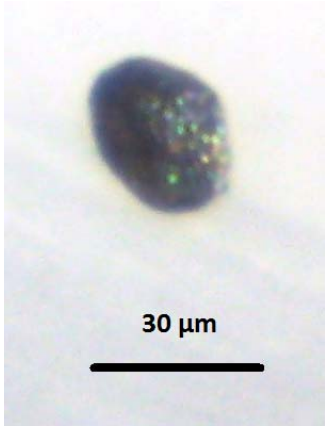


PC-1

PC-2

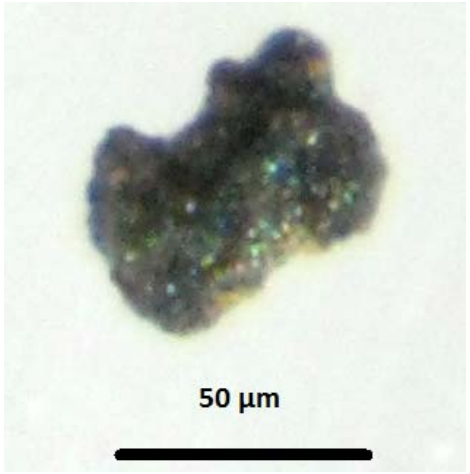
IMAGES OF THULE PARTICLES OBTAINED BY OPTIC MICROSCOPE (II)

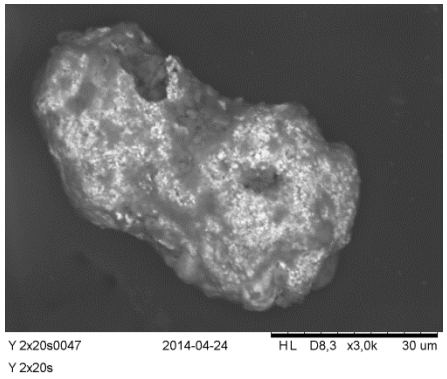
PC-5



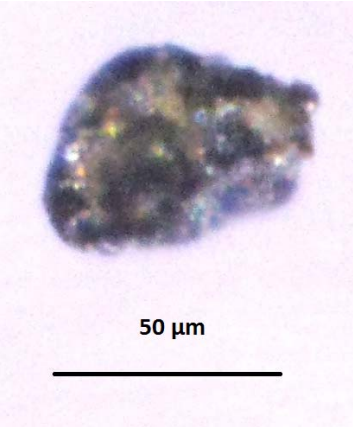
PC-6

PC-4

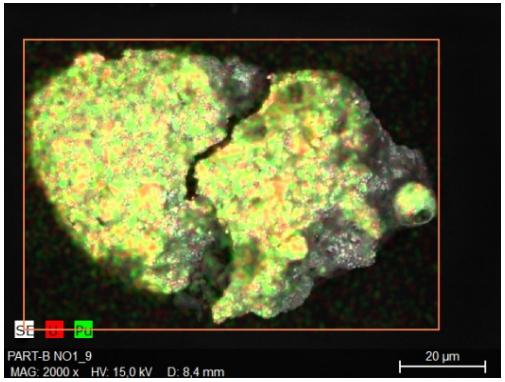




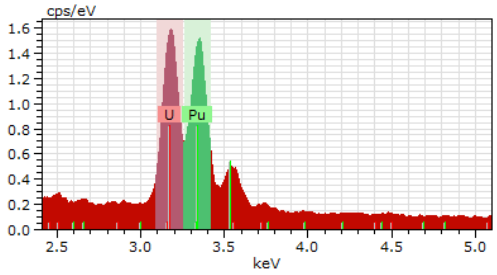
SEM Image of PC-4



PC-7



PC-7



U/Pu ratio ~ 1.3

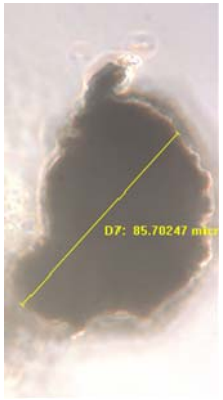
PC-7

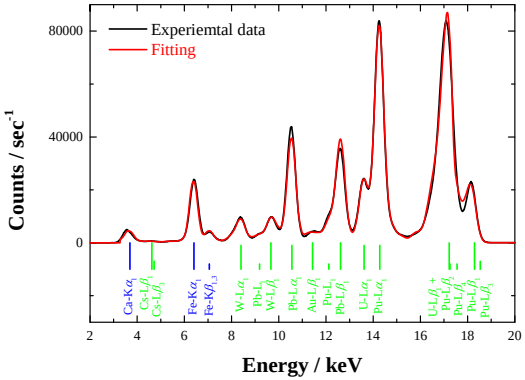
Particle Code	Am-241 [Bq]
PC-1	3.64
PC-2	9.90
PC-4	15.57
PC-5	18.86
PC-6	6.02
PC-7	9.42

Am-241 determinations performed by high-resolution gamma ray spectrometry with Ge detectors

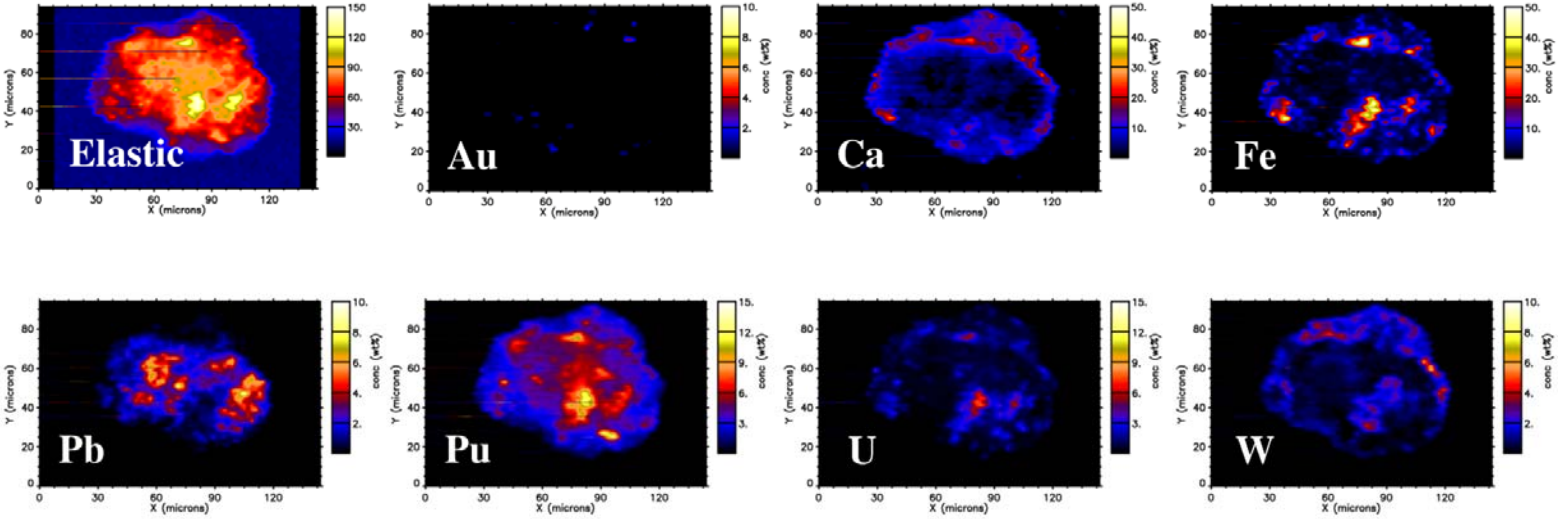
Particles from Conventional Detonations of Nuclear Weapons: Taranaki

Pu non-fission test particle, Maralinga, Australia CODE ID: Mar-Taranaki-3





μ-SR-XRF

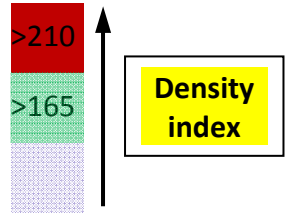


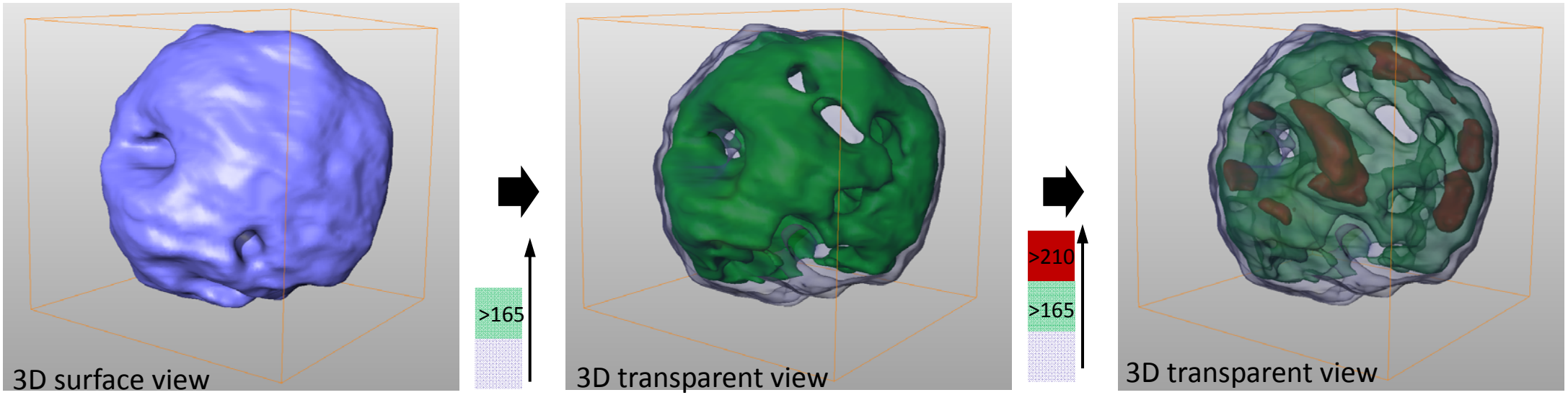
One particle from the Taranaki test site, Maralinga, from non-fission, high explosive tests designed to simulate accident scenarios.

Pu non-fission test particle, Maralinga, Australia CODE ID: M-Tara-A-1

Activity ^{241}Am (Bq)	Size (μm)	Notes
7	20	Fragment, dark

Nano-CT images





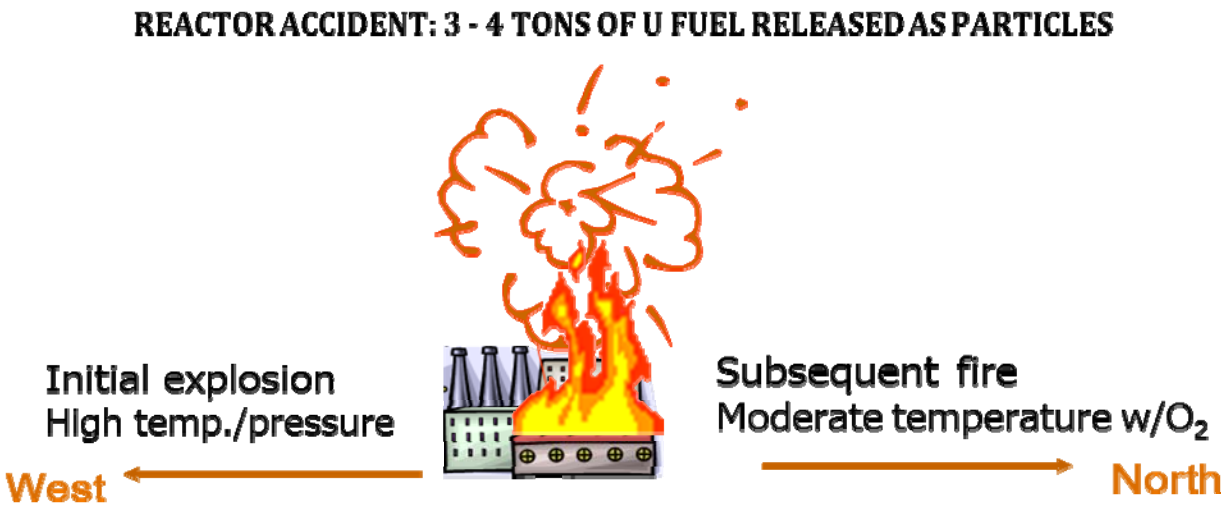
No. of high-density regions (with Max density index 210÷ 255) **: 7**

All high-density regions are inside the sample (not on the surface)

Particles from Nuclear Reactor Accidents: Chernobyl

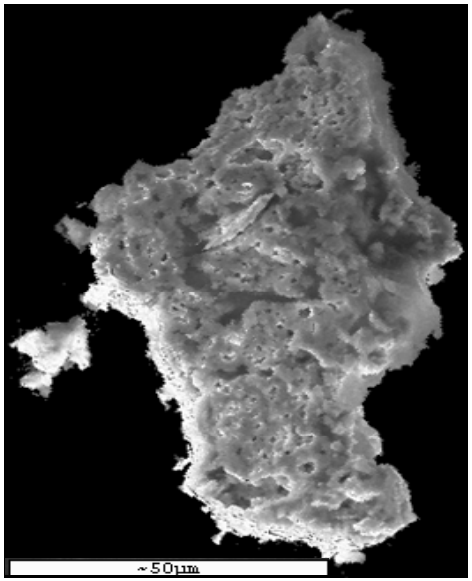
CHERNOBYL PARTICLES

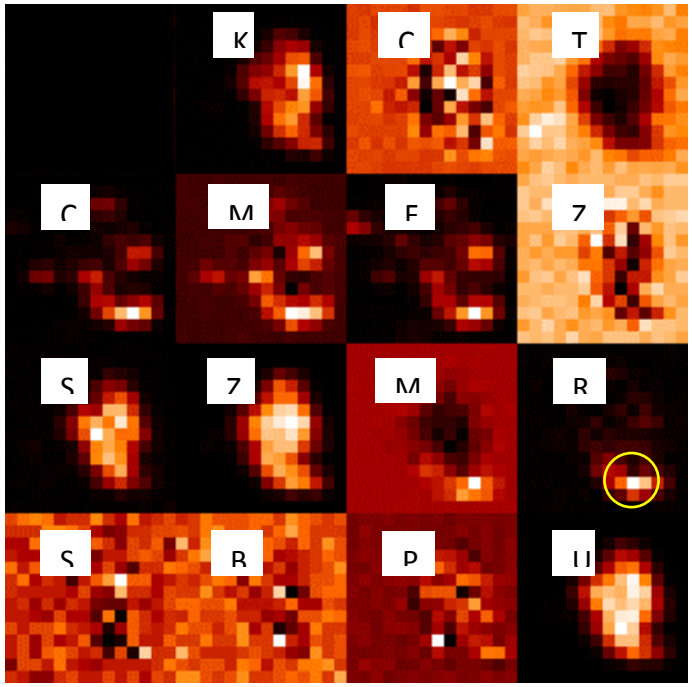
Available Chernobyl particles for transformation studies					
Particle	**Code ID**	**Size (μm)**	**Particle**	**Code ID**	**Size (μm)**
Chernobyl 1 km zone	Iso1 2035	200	Cooling Pond	Ham 414	---
Chernobyl 30 km zone	Ham 6 West	30-150	Cooling Pond	Ham 415a	---
Chernobyl 30 km zone	Ham 41 North	30-150	Cooling Pond	Ham 415b	---



Particles with high radionuclide content: Particle Iso1 2035 contains 2700 Bq of Am-241 and more than 60000 Bq of Cs-137.

SEM and μ-XRF mapping of a Chernobyl U fuel particle carrying radionuclides and stable elements





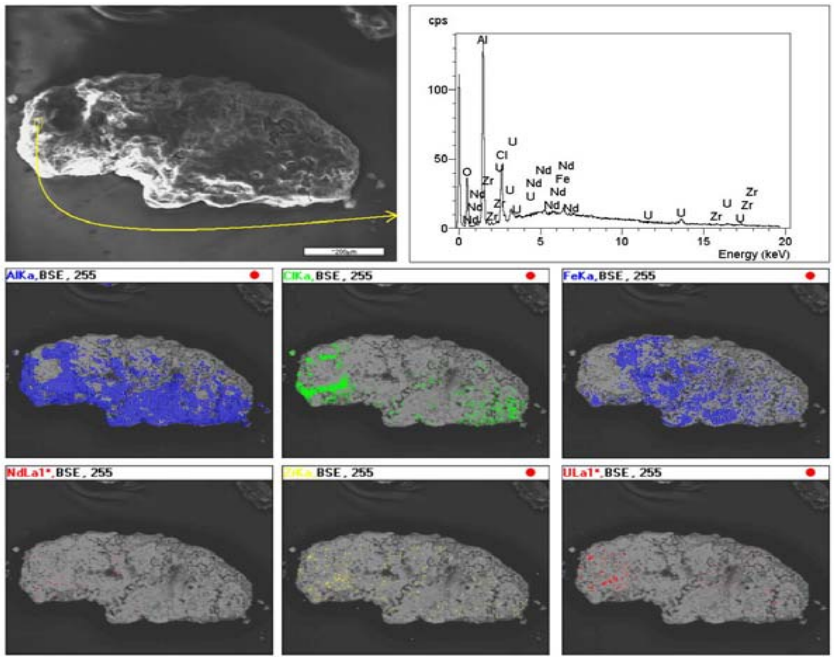
XANES AND XRD results

- West (explosion): **non-oxidised or even reduced forms of U**
- North (fire): UO_2 core surrounded by **oxidised U** (U_2O_5/U_3O_8 layer)

Particles from Accidents nuclear Reprocessing plants: Dounray

A couple of particles from Dounreay (DMTR2, DFR1) are available for transformation studies.

Available Dounray particles for transformation studies		
Code ID	**Size (μm)**	**^{137}Cs (Bq)**
DMTR 2	**1400**	**1.13x 10^{5}**
DFR1	**300**	**1.87x10^{4}**



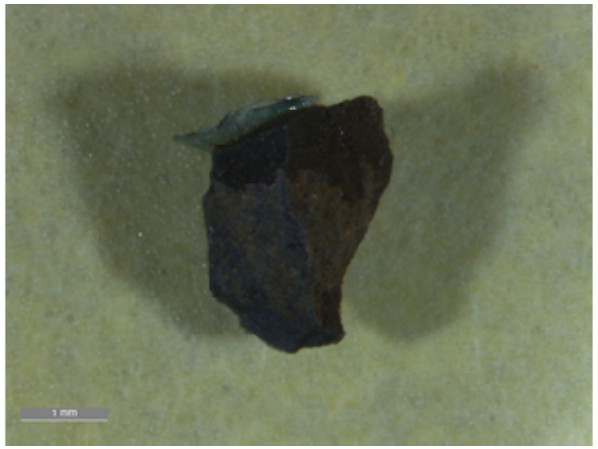
Scanning Electron Microscopy (SEM) and Energy Dispersive X-ray analysis of a Dounreay particle, including X-Ray mapping of several elements

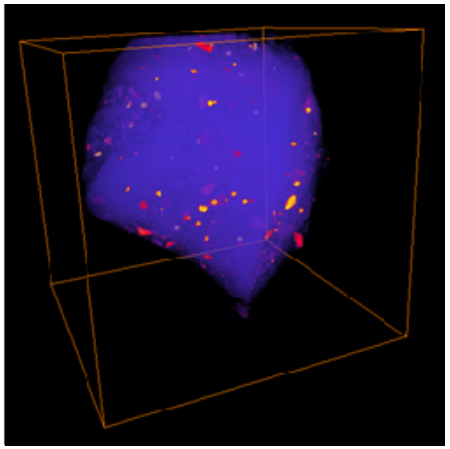
NORM PARTICLES/FRAGMENTS FROM NORWEGIAN NORM SITES
ALUM SHALE

NORM particle/fragment sample ia available from an alun shale (rich in U) tunnel construction area at Gran, Hadeland, Norway (RV4),

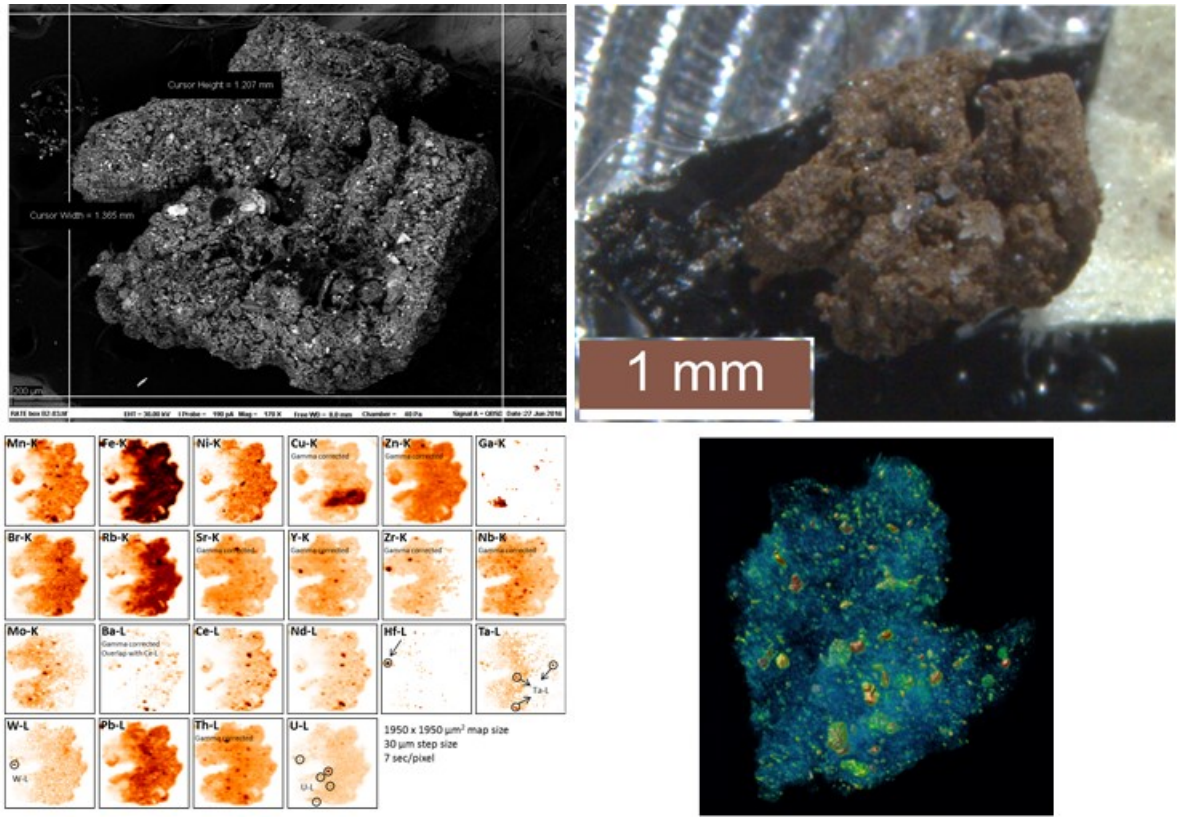
Available Alum shale fragment for transformation studies		
Particle	**CODE ID**	**Size (μm)**
Gran tunnel construction area (RV4), Hadeland	**RV4 surface 1**	**~4000**

Light microscope (left) of an alun shale fragment with heterogeneous distributions as demonstrated by nanotomography (right).





NORM PARTICLES/FRAGMENTS FROM NORWEGIAN NORM SITES
FEN/SOVE TH RICH AREA



Characterization of sample HAM365b from the Fen NORM site, Telemark, Norway.

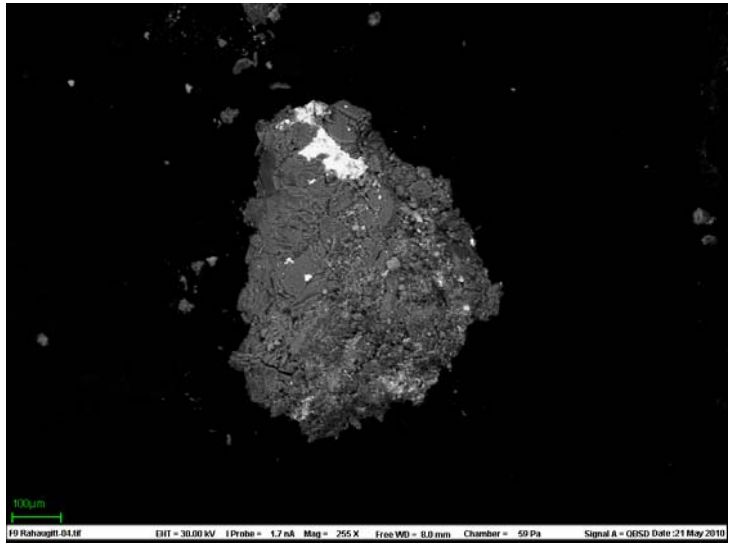
ESEM-EDX (top eft), light microscopy (top right), SR based micro-XRF (bottom left) and nano-CT (bottom right) demonstrate a large mineral grain with a very heterogeneous distribution of densities and elements.

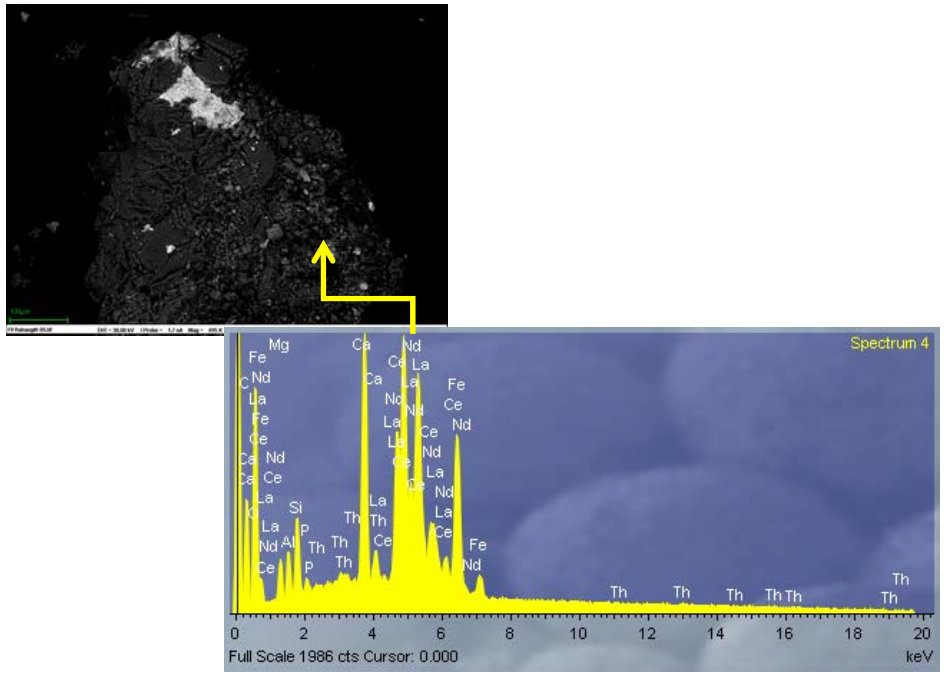
NORM PARTICLES/FRAGMENTS FROM NORWEGIAN NORM SITES
FEN/SOVE TH RICH AREA

A total of 8 particles/fragments from Fwen/Sove are available and have been characterized by SEM-EDX and Sr based micro-XRF. One example is shown in previous page (Ham 365 b)

CODES ID: HAM 269, Ham 362, Ham 364, Ham 365b, Ham 416, Ham 417, Ham 418, Ham 419

PARTICLES ENRICHED IN RARE-EARTHS

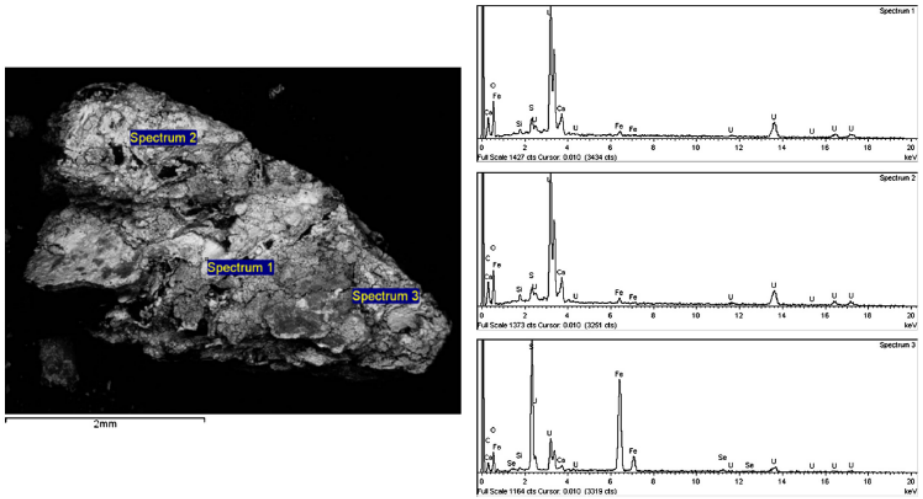




NORM PARTICLES FROM U-MINING

A couple of particles from the Kadji sai U mine, Kyrgyzstan are available for the transformation studies. Some details of these or similar particles can be found in (Lind et al., 2013; Lind, 2011).

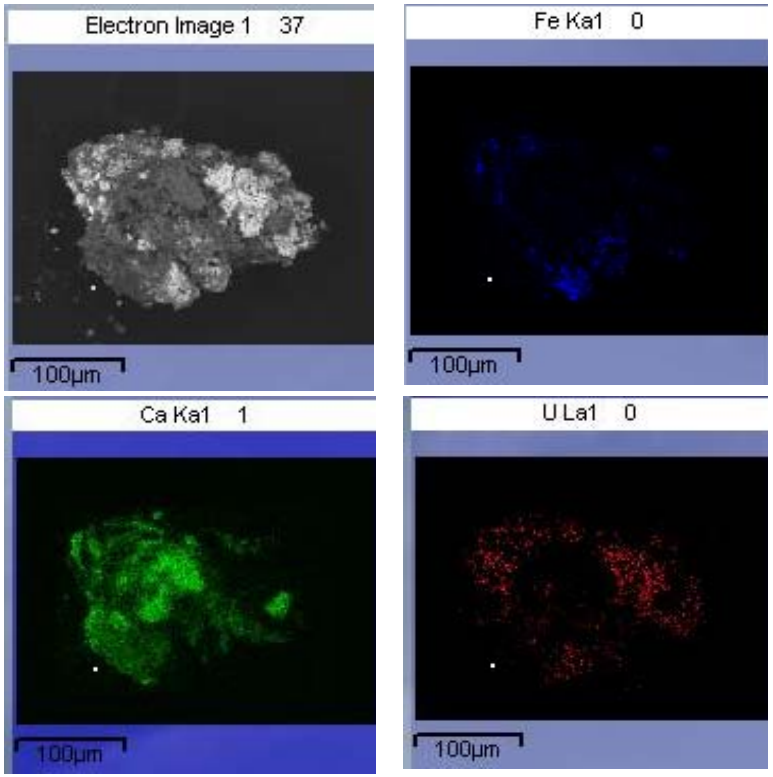
Available U-mining particles for transformation studies		
Particle	**CODE ID**	**Size (μm)**
Kadji sai U mine Kyrgyzstan	**Ham 228**	**150**
Kadji sai U mine Kyrgyzstan	**Ham 240**	**1500**

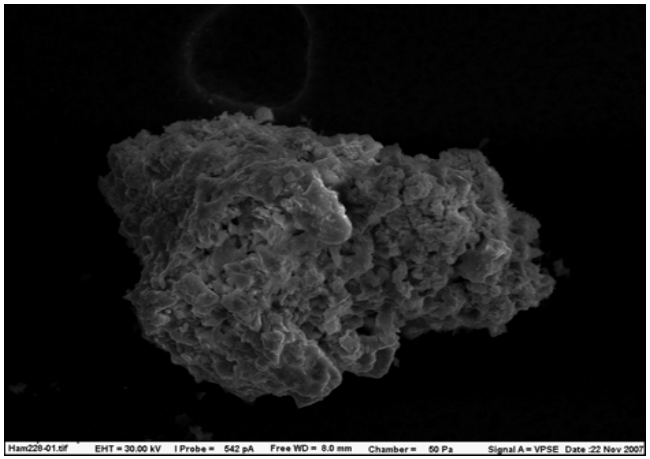


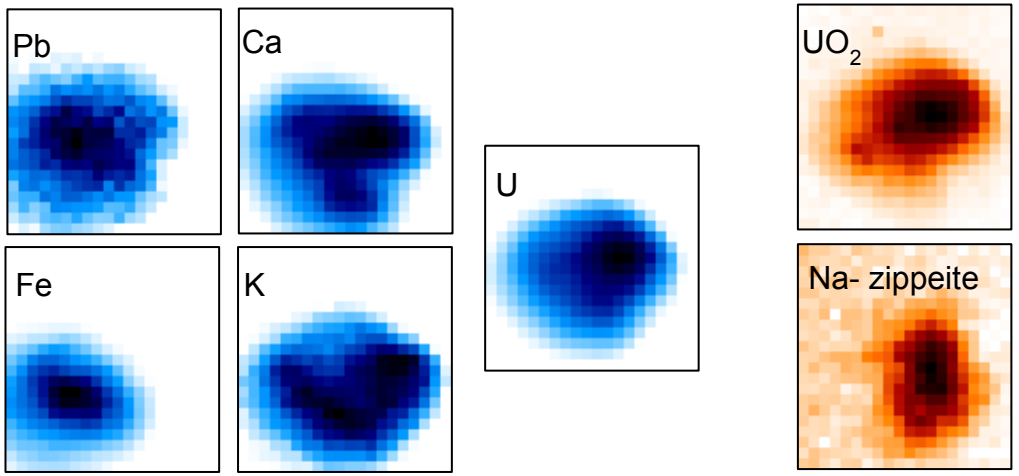
ESEM-EDX of a mineral grain collected from the Kadji Sai area near the abandoned mine. Electron micrograph recorded in backscattered electron imaging mode (upper left). Bright areas reflect high atomic number areas on the surface of the specimen. ESEM-EDX spectra from the bright areas show that U was a major element in the mineral grain.

Kadji sai U mine

Ham 228







ESEM-EDX

µ-XRF-mapping

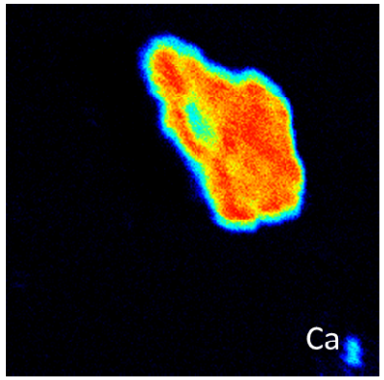
µ-XRD-mapping

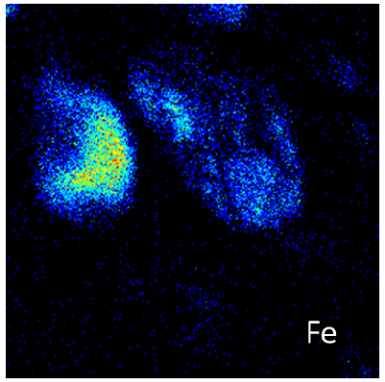
Kadji sai U mine

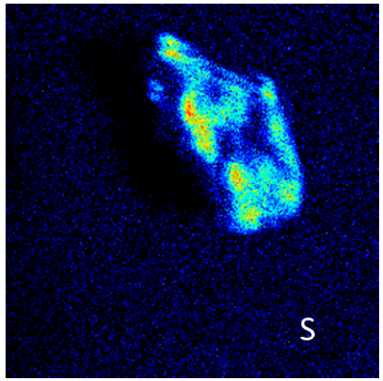
Ham 228

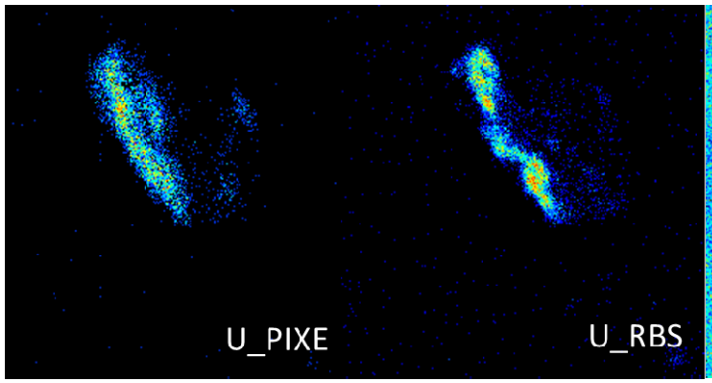
μ- PIXE analysis

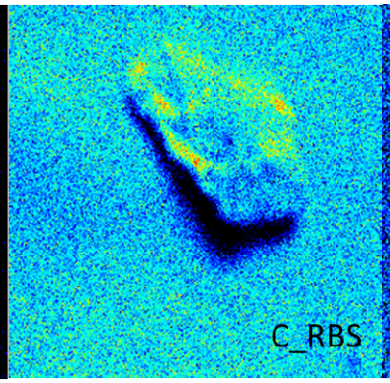
Scan: 500*500 um²
Acquisition time: 153.4 min

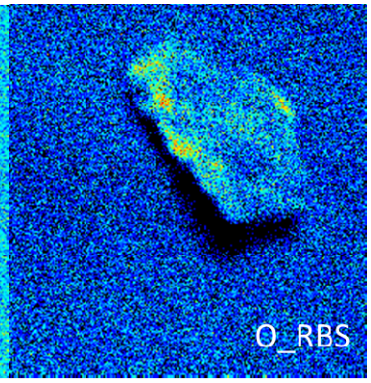


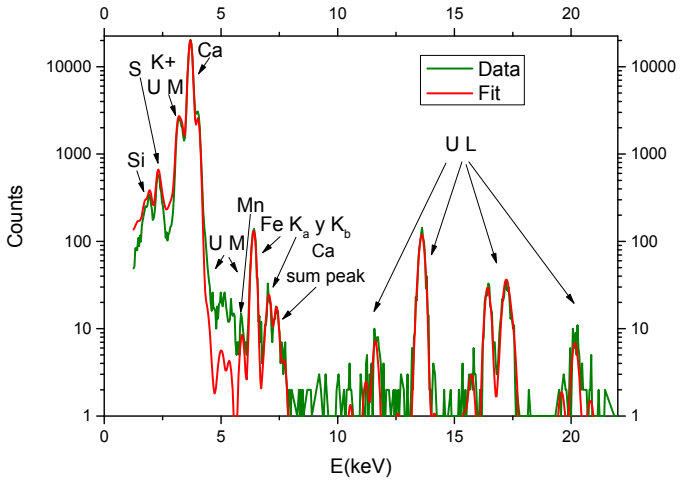








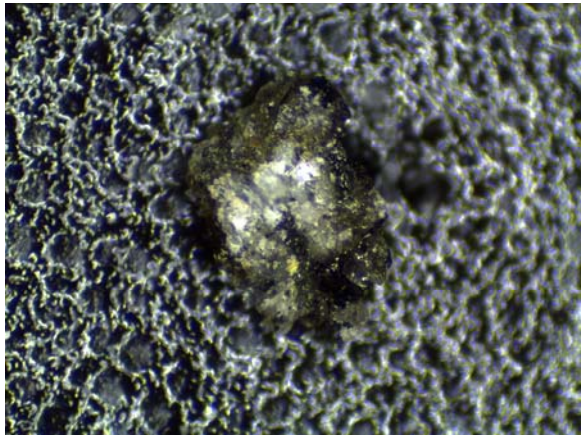




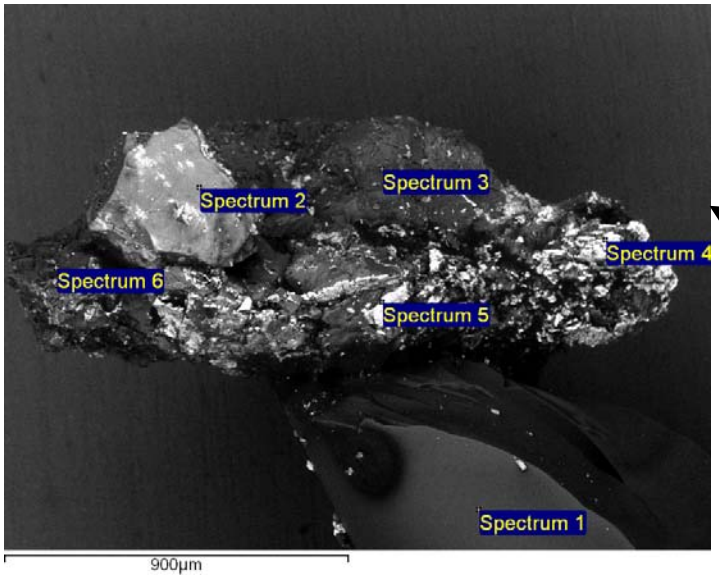
Point	U (%)
1	21.3
2	23.1
3	27.5
4	20.9
5	21.7
6	19.3

Kadji sai U mine

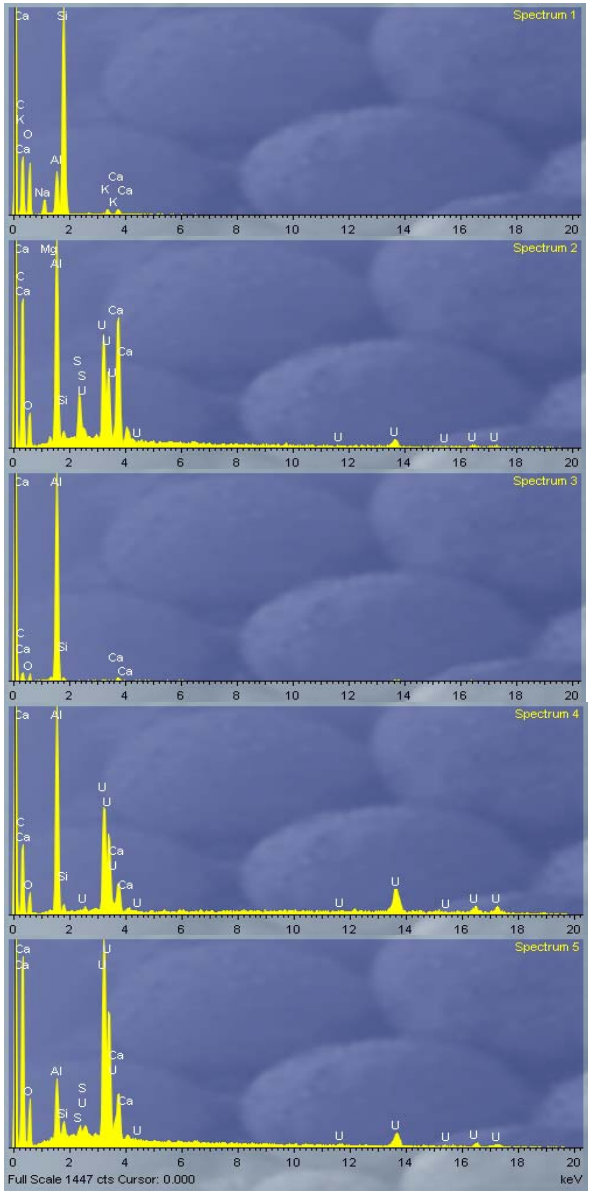
Ham 240

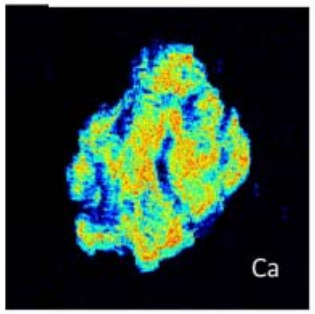


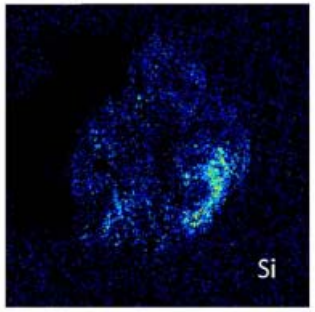
Optic Microscope

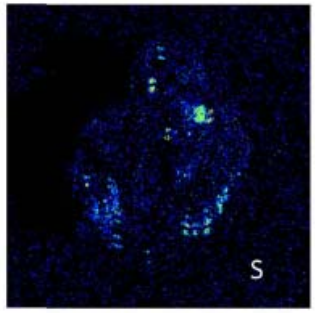


SEM -EDX



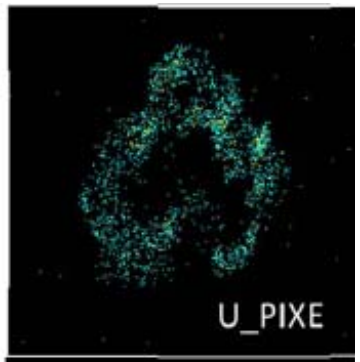


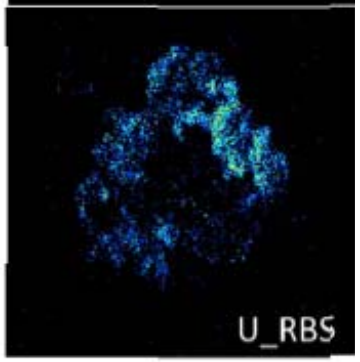




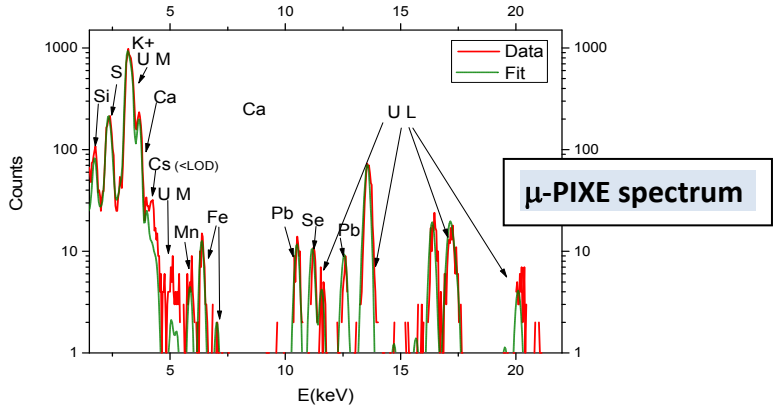
Kadji sai U mine

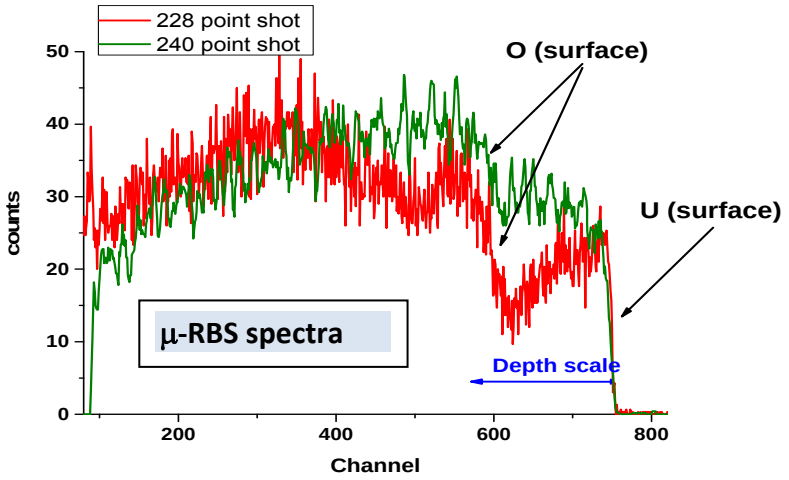
Ham 240



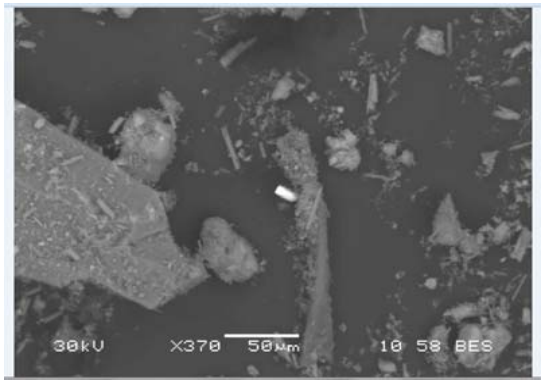


μ-PIXE & μ-RBS ANALYSIS

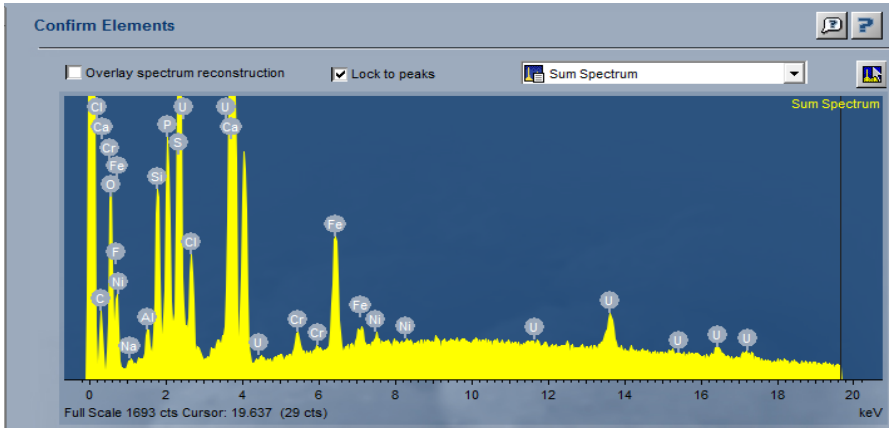




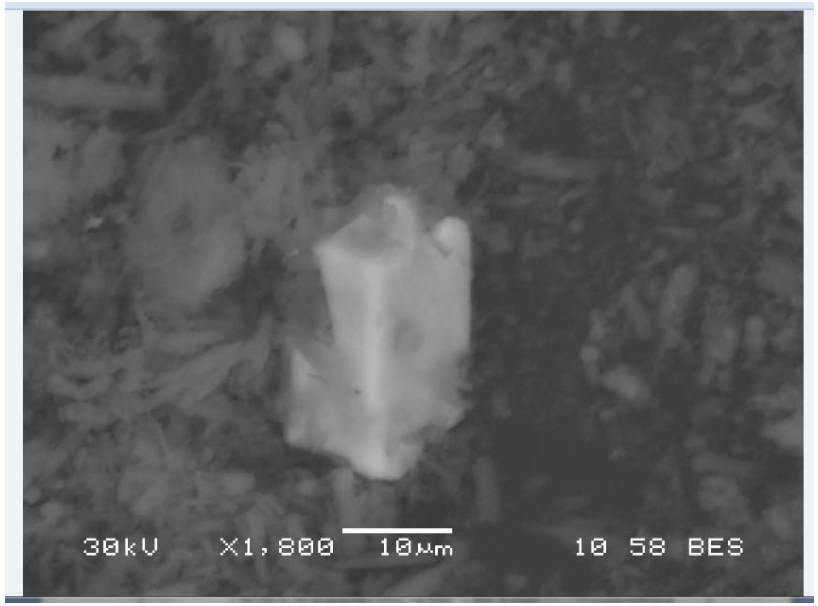
NORM PARTICLES PHOSPHATE INDUSTRY
Particle 1, CODE ID: FERTI-1

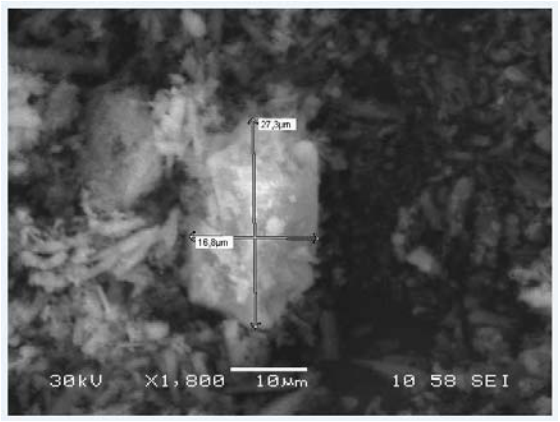


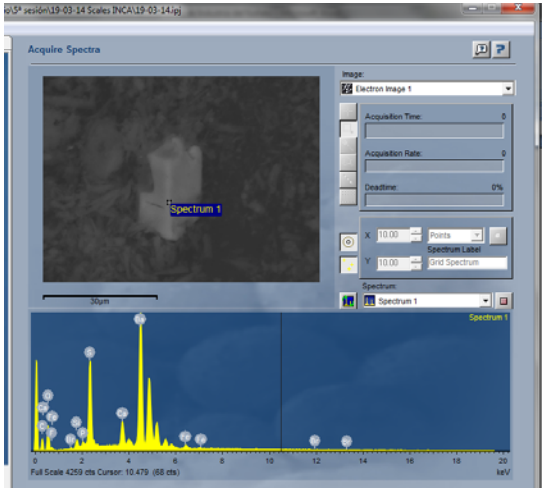
Tabular shape, with a maximum length of 20 µm.
SEM-EDX indicates that its majority compound is U.



NORM PARTICLES PHOSPHATE INDUSTRY
Particle 2, CODE ID: FERTI-2

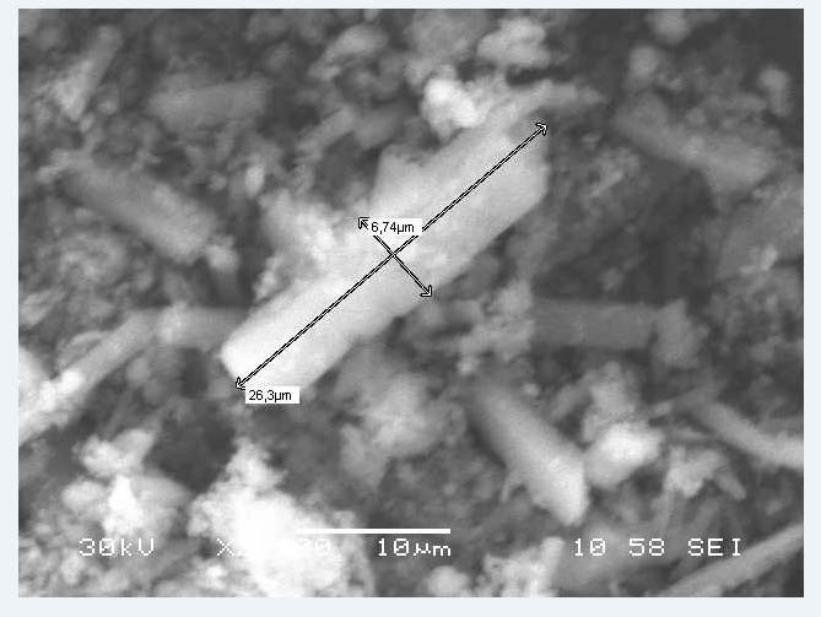


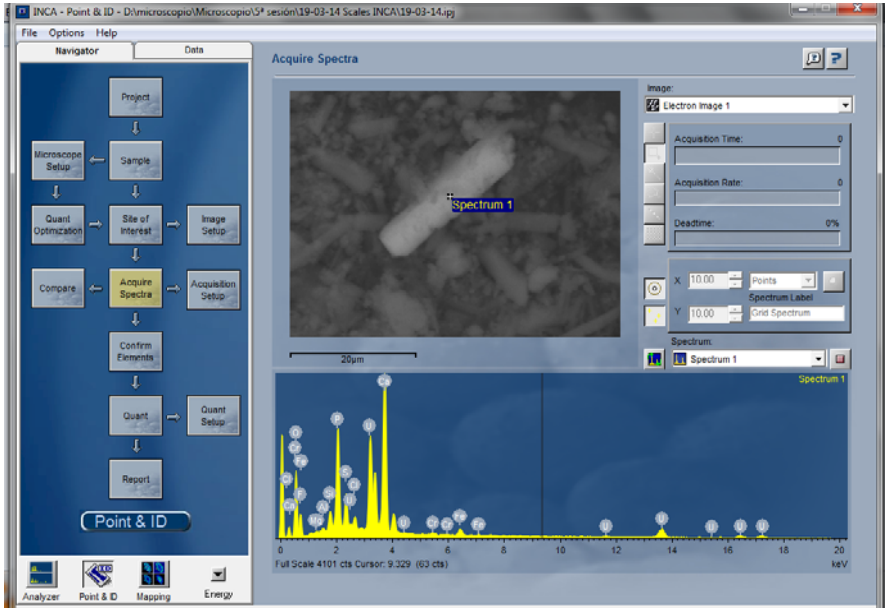




Small hot-particle found in the filtration unit. Polygonal structure, is mainly formed by U, as was deduced from SEM-EDX analysis

NORM PARTICLES PHOSPHATE INDUSTRY
Particle 3, CODE ID: FERTI-3



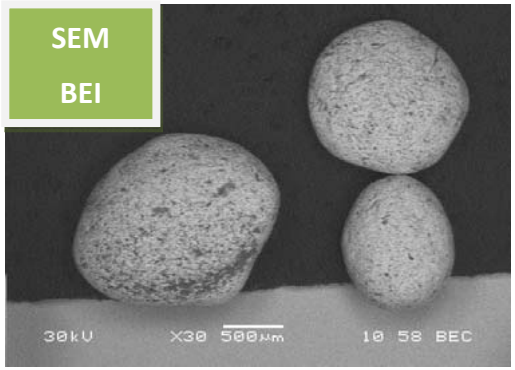


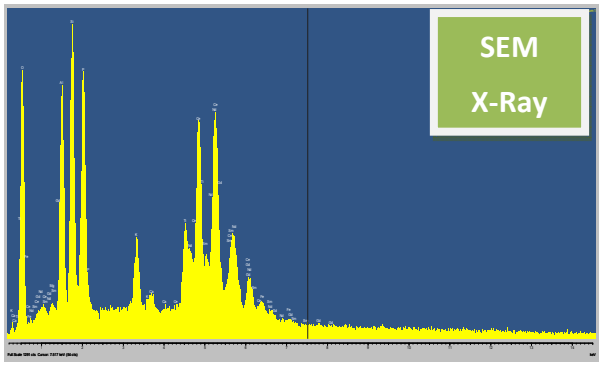
Hot particle with cylindrical and regular shape. Near 30 µm maximum length. EDX analysis indicates that is majority element is U.

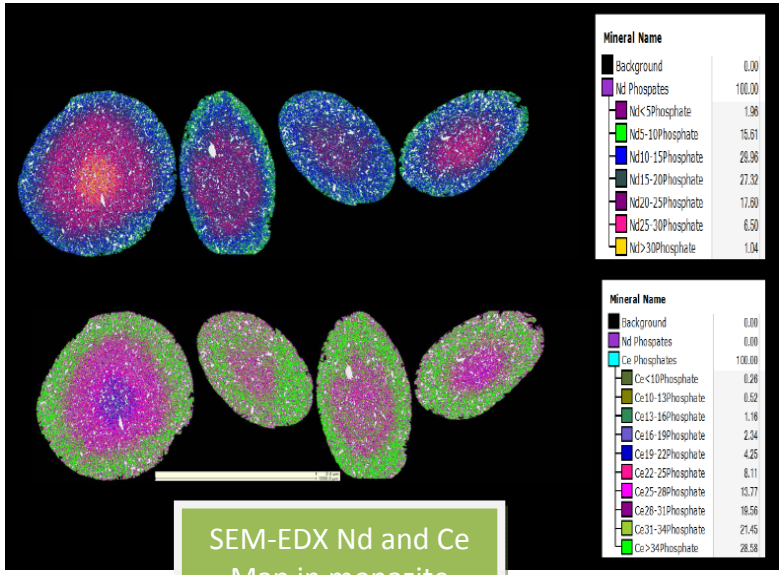
In the phosphate industry is also possible to find hot particles formed mainly by ^{226}Ra and Ba. Not included in this database because are out of the scope of the project.

NORM PARTICLES MONAZITE

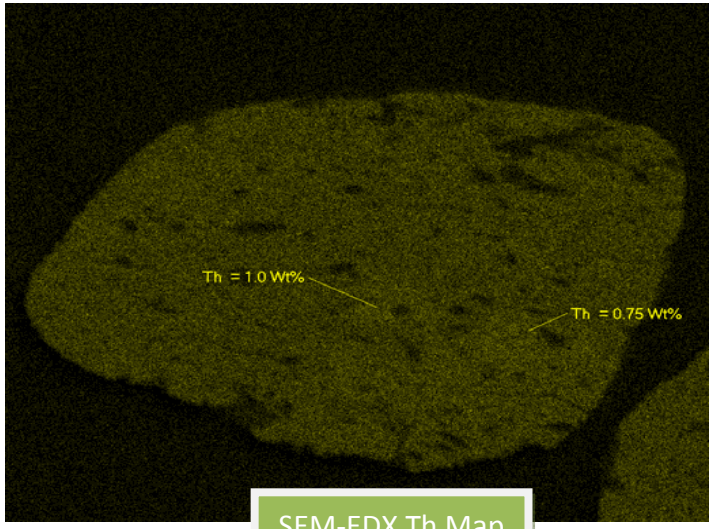
Optic Microscope Image







SEM-EDX Nd and Ce Map in monazite



SEM-EDX Th Map in monazite