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# DISSERTATION

Investigation of the  $^{236}\text{U}$  occurrence in the environment

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The ability to perform classical  $\alpha$ -radioanalyses successfully is partly  
a personal one requiring relatively rare experimental skill,  
the benefits of patience and discipline and perhaps  
a little magic.

(Crawford et al., 1978)



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## Abstract

This work deals with the natural and anthropogenic occurrence of  $^{236}\text{U}$  in our environment. For this reason samples from representative sites were measured for their  $^{236}\text{U}/^{238}\text{U}$  isotopic ratios by Accelerator Mass Spectrometry (AMS).

$^{236}\text{U}$  with a half life of  $2.3 \times 10^7$  years is naturally produced via thermal neutron capture on  $^{235}\text{U}$  in ultra-trace amounts in ores, soils and rocks. Additionally a huge content has been produced in nuclear power plants by the same way as in nature via  $^{235}\text{U}(\text{n},\gamma)^{236}\text{U}$  and from nuclear weapons tests via  $^{238}\text{U}(\text{n},3\text{n})^{236}\text{U}$ . Thus  $^{236}\text{U}$  is a useful fingerprint to detect anthropogenic sources in the environment and, on the other hand, if an anthropogenic contribution can be excluded, the natural signal could be used for geological applications.

The natural fraction of  $^{236}\text{U}$  was analysed in uranium ore and yellow cake samples. Furthermore environmental samples (natural water and soils), where it was expected to find a natural isotopic ratio of  $^{236}\text{U}/^{238}\text{U}$ , were investigated. In order to cover anthropogenic  $^{236}\text{U}$  in the environment, contaminated sediment samples from the Irish Sea were analysed. In addition the feasibility to use ionic liquids for the extraction of uranium from aqueous solution was tested to simplify the sample preparation for larger water volumes.

In uranium ore and yellow cake samples of known geographic origin (Australia, Brazil and Canada) the natural  $^{236}\text{U}/^{238}\text{U}$  isotopic ratio was investigated. Due to this special isotopic ratio a possible correlation between the original mineral (uranium ore) and the intermediate product (yellow cake) was studied. Such relations are useful indicators for nuclear forensic or for non-proliferation purposes. Furthermore three pre-nuclear materials were analysed for their  $^{236}\text{U}/^{238}\text{U}$  isotopic ratio to answer the question whether these samples had been irradiated in the past.

Water samples (up to 5 L) from rivers, creeks and wells were collected in the alpine region of Forstau (Salzburg, Austria) and from surrounding areas to investigate the probable natural background. The  $^{238}\text{U}$  concentration was measured by alpha spectrometry using  $^{232}\text{U}$  as a yield tracer. Moreover water samples from Slovakia and Slovenia were analysed and finally some additional water samples from Austria (25 L and more). The measurements of  $^{236}\text{U}$  in natural water samples from rivers, creeks and wells have shown the dispersion of anthropogenic  $^{236}\text{U}$  in the environment far away from local contamination sources.

Furthermore uranium and plutonium were investigated in soil samples from La Palma (Canary Island) by alpha spectrometry. Additionally these fractions were measured by AMS to get information on the isotopic ratios  $^{236}\text{U}/^{238}\text{U}$ ,  $^{240}\text{Pu}/^{239}\text{Pu}$  and  $^{236}\text{U}/^{239}\text{Pu}$ , respectively. It is well known from the literature that the isotopic ratio  $^{240}\text{Pu}/^{239}\text{Pu}$  is a very useful tool to assess the source of anthropogenic contamination. Due to this Pu isotopic ratio it was possible to verify that the samples show a global fallout signature. Consequently  $^{236}\text{U}$  could be assigned to the same origin.

Marine sediment samples from the Irish Sea were analyzed for the isotopic composition of uranium, plutonium and americium by a combination of radiometric methods and AMS. This part of the work shows the possibility to use  $^{236}\text{U}$  for the identification of anthropogenic uranium. In addition the isotopic ratio  $^{241}\text{Am}/^{243}\text{Am}$  was for the first time measured via AMS and compared with alpha spectrometry measurements.

For determining the natural level of  $^{236}\text{U}$  with its environmental abundance of  $10^{-10} - 10^{-8} \%$  in natural water samples rather large sample volumes ( $\sim 30 \text{ L}$ ) are necessary. Therefore the conventional radiochemical uranium analysis (pre-concentration or co-precipitation followed by column chromatography) is very time-consuming. To shorten the procedure hydrophobic ionic liquids (ILs) were tested for the extraction of uranium from aqueous solutions. High selectivity and efficiency for uranium compared to divalent calcium and magnesium in a natural water matrix was achieved with tricaprylmethylammonium thiosalicylate, [A336][TS]. Stripping of uranium from this IL with  $2\text{M HNO}_3$  was successfully achieved.

To sum up this comprehensive work presents on the one hand an overview about the natural and anthropogenic occurrence of  $^{236}\text{U}$  in different sample matrices and on the other hand the applicability of ionic liquids to extract uranium from aqueous solutions.

## Zusammenfassung

Diese Arbeit handelt über das natürliche und anthropogene Vorkommen von  $^{236}\text{U}$  in unserer Umwelt. Aus diesem Grund wurden Proben von speziell ausgewählten Standorten auf ihr  $^{236}\text{U}/^{238}\text{U}$  Isotopenverhältnis mittels Beschleuniger-Massenspektrometrie (AMS) untersucht.

$^{236}\text{U}$  besitzt eine Halbwertszeit von  $2.3 \times 10^7$  Jahren und wird in der Natur in Spuren über Neutroneneinfang aus  $^{235}\text{U}$  in Erzen, Boden und Gestein produziert. Zusätzlich wird es, genau wie in der Umwelt, in großen Mengen in Kernkraftwerken über  $^{235}\text{U}(n,\gamma)^{236}\text{U}$  und möglicherweise in Kernwaffen über  $^{238}\text{U}(n,3n)^{236}\text{U}$  gebildet. Aus diesem Grund gilt  $^{236}\text{U}$  als potentieller „Fingerprint“ für anthropogene Quellen in der Natur und andererseits könnte ein ausschließlich natürliches Vorkommen für geologische Anwendungen genützt werden.

Beginnend mit Uranerzen und Yellow Cake Proben, welche natürliches  $^{236}\text{U}$  beinhalten, wurden weiters Umweltproben (natürliche Gewässer und Bodenproben), bei denen erwartet wurde ein natürliches  $^{236}\text{U}/^{238}\text{U}$  Isotopenverhältnis zu finden, untersucht. Um anthropogenes  $^{236}\text{U}$  in der Umwelt zu untersuchen, wurden kontaminierte Sedimentproben aus der Irischen See analysiert. Zusätzlich wurde die Möglichkeit, Ionische Flüssigkeiten zur Uranextraktion aus wässrigen Lösungen zu verwenden, getestet, um eine Vereinfachung der Probenvorbereitung für große Wasservolumina zu ermöglichen.

In Uranerzen und Yellow Cake Proben von bekannter Herkunft (Australien, Brasilien und Kanada) wurde das natürliche Isotopenverhältnis  $^{236}\text{U}/^{238}\text{U}$  ermittelt. Aufgrund dieses speziellen Isotopenverhältnisses wurde eine mögliche Korrelation zwischen dem Ausgangsprodukt (Uranerz) und dem Zwischenprodukt (Yellow Cake) untersucht. Solche Zusammenhänge sind nützliche Hinweise für die nukleare Forensik und für die Nichtverbreitung von Kernwaffen. Weiters wurden drei Materialien, die aus dem prä-nuklearen Zeitalter stammen, auf ihr  $^{236}\text{U}/^{238}\text{U}$  Verhältnis untersucht, um zurückzuschließen, ob diese Proben in der Vergangenheit bestrahlt worden sind.

Wasserproben (bis zu 5 L) wurden von Flüssen, Bächen und Brunnen aus der alpinen Gegend in Forstau (Salzburg, Österreich) und dessen Umgebung auf einen möglichen natürlichen Hintergrund untersucht. Die  $^{238}\text{U}$  Konzentration wurde mittels Alphaspektrometrie bestimmt und für die Bestimmung der Ausbeute wurde ein  $^{232}\text{U}$  Spike verwendet. Weiters wurden Wasserproben aus der Slowakei und Slowenien als auch aus Österreich (25 L und mehr) analysiert. Die  $^{236}\text{U}$  Messungen von natürlichen Gewässern, wie von Flüssen, Bächen und Brunnenwasser, zeigt die Ausbreitung an anthropogenem  $^{236}\text{U}$  in der Umwelt weit entfernt von lokal kontaminierten Ausgangspunkten.

Uran und Plutonium wurden des Weiteren in Bodenproben von La Palma (Kanarische Insel) mittels Alphaspektrometrie untersucht. Zusätzlich wurden, um Informationen über die Isotopenverhältnisse  $^{236}\text{U}/^{238}\text{U}$ ,  $^{240}\text{Pu}/^{239}\text{Pu}$  beziehungsweise  $^{236}\text{U}/^{239}\text{Pu}$  zu erhalten, diese Fraktionen mit Hilfe von AMS gemessen. Aus der Literatur ist bekannt, dass das Isotopenverhältnis  $^{240}\text{Pu}/^{239}\text{Pu}$  ein sehr wertvolles Hilfsmittel ist, um die Herkunft der anthropogenen Kontamination ermitteln zu können. Es konnte anhand dieses Pu Isotopenverhältnisses gezeigt werden, dass die Proben eine Global Fallout Signatur aufweisen. Somit war es möglich,  $^{236}\text{U}$  derselben Herkunft zuzuordnen.

Marine Sedimentproben aus der Irischen See wurden auf ihre Uran, Plutonium und Americium Isotopenzusammensetzung mittels einer Kombination aus radiometrischen Methoden und AMS untersucht. Dieser Teil der Arbeit zeigt die Möglichkeit,  $^{236}\text{U}$  für die Identifizierung von anthropogenem Uran zu verwenden. Weiters wurde zum ersten Mal das Isotopenverhältnis  $^{241}\text{Am}/^{243}\text{Am}$  mit AMS gemessen und mit den Ergebnissen der Alphaspektrometrie verglichen.

Für die Bestimmung des natürlichen  $^{236}\text{U}$ , mit einer Häufigkeit von  $10^{-10} - 10^{-8} \%$  in natürlichen Wasserproben, sind ziemlich große Probenvolumina ( $\sim 30 \text{ L}$ ) notwendig. Aus diesem Grund ist die konventionelle radiochemische Urananalyse (aufkonzentrieren oder mitfällen mit nachfolgender Säulenchromatographie) sehr zeitaufwendig. Um diese Prozedur zu beschleunigen, wurden hydrophobe Ionische Flüssigkeiten als potentielles Extraktionsmittel für Uran aus wässrigen Lösungen ermittelt. Eine hohe Selektivität und Effizienz für Uran verglichen mit zweiwertigem Calcium und Magnesium wurden bei einer Abtrennung aus einer natürlichen Wassermatrix mit Tricaprylmethylammoniumthiosalicylat, [A336][TS] erzielt. Uran wurde erfolgreich aus dieser Ionischen Flüssigkeit mittels  $2\text{M HNO}_3$  zurückextrahiert.

Zusammenfassend lässt sich sagen, dass die vorliegende Arbeit einerseits einen Überblick über das natürliche und anthropogene Vorkommen von  $^{236}\text{U}$  in unterschiedlichen Probenmatrices bietet und andererseits die Anwendbarkeit von Ionischen Flüssigkeiten für die Uranextraktion aus wässrigen Lösungen vorstellt.

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## 1. Introduction

In 1896 H. Becquerel found that crystals of potassium uranyl sulphate wrapped in paper were able to produce black spots on photographic plates after they had been exposed to sunlight. But the same phenomenon also occurred with assemblies which had not been exposed to light and the uranyl salt seemed to produce radiation spontaneously. It was the discovery of the natural radioactivity. Afterwards M. Curie showed that U and Th compounds produced ionizing radiation independent of the chemical composition of the salt. Additionally she discovered that uranium minerals like pitchblende produced more ionizing radiation than the same amount of pure metallic uranium. She had the suspicion that more active elements than uranium were present in these minerals. Together with her husband, P. Curie, they purified large amounts of pitchblende and finally were able to isolate a substance which they named polonium. In the same year (1898) they, together with G. Bemont, isolated another radioactive substance which they called radium [1]. In 1903 H. Becquerel, M. and P. Curie received the physics noble prize for the discovery of the radioactivity. Eight years later, in 1911, M. Curie got the chemistry noble prize for the discovery of Po and Ra and the investigation of Ra chemistry.

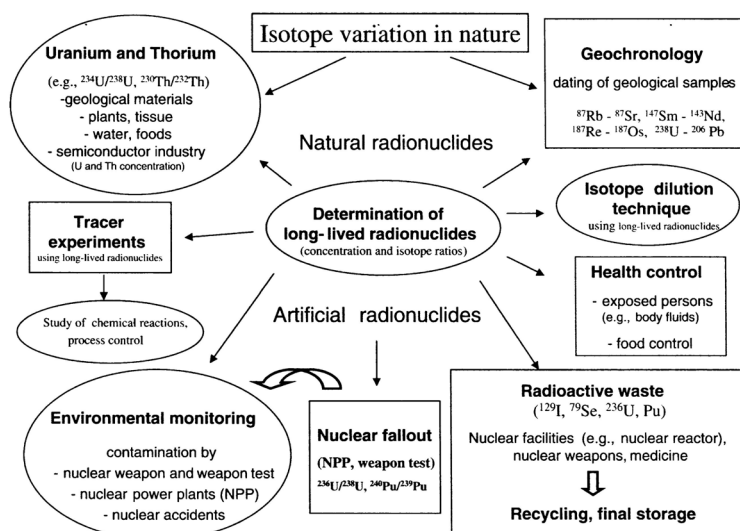
Today we know that radionuclides occur both naturally and anthropogenically in our environment. They can be divided in those produced by cosmic radiation (categorized as cosmogenic), nuclides with very long half lives, e.g.  $^{238}\text{U}$ ,  $^{235}\text{U}$  and  $^{232}\text{Th}$  (comparable to the age of the earth and known as primordial radionuclides) and nuclides which are part of the natural decay chain of these progenitors (called radiogenic nuclides), and finally, those radionuclides which were introduced in nature due to man's activity and accidents (referred to as anthropogenic) [2].

The cosmic radiation originates in space and interacts mainly with carbon, nitrogen and oxygen [3]. Examples for cosmogenic radionuclides are  $^3\text{H}$  (12.3 years),  $^{14}\text{C}$  (5730 years) and  $^{10}\text{Be}$  ( $1.6 \times 10^6$  years).

Primordial radionuclides are produced in stellar nucleosynthesis and have persisted since the formation of the earth because their half lives are longer than  $10^8$  years. Typical examples for primordial radionuclides are  $^{235}\text{U}$  ( $7.0 \times 10^8$  years),  $^{238}\text{U}$  ( $4.5 \times 10^9$  years),  $^{232}\text{Th}$  ( $1.4 \times 10^{10}$  years) and  $^{40}\text{K}$  ( $1.3 \times 10^9$  years) [4]. Actinides, especially uranium and thorium, are omnipresent in nature and their existence has been known since a long time ago but the use of actinides got to a new level with the discovery of nuclear fission in 1938. Nuclear fission can be used both

peaceful (e.g. as an energy source) and for military purposes (e.g. nuclear weapons); the latter resulted in a global spread of anthropogenic radionuclides in the environment. Fallout from nuclear weapons testing is the major source of transuranic elements, especially of plutonium [5]. Due to the detonation of atmospheric weapons test anthropogenic Pu is ubiquitous. The testing of thermonuclear devices, which started in 1952, produced the highest amount of airborne Pu [6]. Uranium, on the other hand, is omnipresent and occurs naturally at different concentrations. Due to its high abundance in the Earth's crust of around 3 ppm, natural U in the environment dilutes anthropogenic uranium which can be detected by small variation in the  $^{235}\text{U}/^{238}\text{U}$  ratio (natural value is 0.00725) and the presence of  $^{236}\text{U}$  [7]. To distinguish natural from anthropogenic uranium,  $^{236}\text{U}$  or the isotopic ratio  $^{236}\text{U}/^{238}\text{U}$  is more effective as an indicator than the  $^{235}\text{U}/^{238}\text{U}$  ratio. The deviation of the  $^{235}\text{U}/^{238}\text{U}$  ratio from the natural value cannot always give conclusive information because the  $^{235}\text{U}$  enrichment and therefore the  $^{235}\text{U}/^{238}\text{U}$  ratio in spent fuel can vary significantly [8]. The advantage of  $^{236}\text{U}$  is the large dynamic range between the natural and anthropogenic  $^{236}\text{U}/^{238}\text{U}$  isotopic ratio (see section 1.2).

The analysis and measurement of unstable isotopes in different sample types are very important for various applications, e.g. nuclear industry, radioactive waste management and disposal as well as in health physics, geology, geochronology and environmental science. Due to this, there are several applications for the measurements of isotopic ratios and they are summarized in Figure 1.



**Figure 1.** Possible application fields for the determination of long lived radionuclides [9].

In the following subsections the elements which were investigated during this work are described. A brief overview is given about uranium with a following emphasis on  $^{236}\text{U}$ . Furthermore a survey about plutonium and americium is given.

## 1.1 Uranium

Uranium was discovered by M.H. Klaproth (1789) in a pitchblende specimen which is an impure uranium oxide consisting of  $\text{UO}_2$  and  $\text{U}_3\text{O}_8$ . The principal use of this element during the first century (after its discovery) was as colorant for ceramics and glasses. As already mentioned in 1896 H. Becquerel discovered that uranium emits penetrating rays [10]. Uranium, as it occurs in nature, consists of four isotopes: the primordial nuclides  $^{238}\text{U}$  (99.2747% by mass) and  $^{235}\text{U}$  (0.7200%), the radiogenic  $^{234}\text{U}$  (0.0054%) and traces of  $^{236}\text{U}$  [11]. The isotopes of interest are listed in Table 1 and the data used are from nucleonica [12].

**Table 1.** Nuclear properties of U isotopes

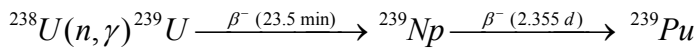
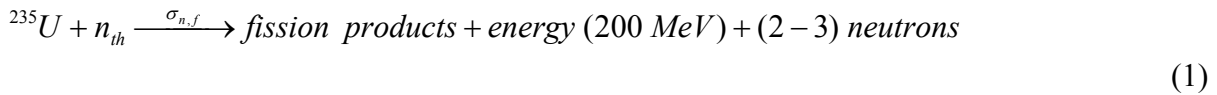
| Isotope          | Half life [a]       | Energy [MeV] | Abundance [%] |
|------------------|---------------------|--------------|---------------|
| $^{234}\text{U}$ | $2.455 \times 10^5$ | 4.775        | 71.38         |
|                  |                     | 4.722        | 28.42         |
| $^{235}\text{U}$ | $7.038 \times 10^8$ | 4.398        | 55            |
|                  |                     | 4.366        | 17            |
| $^{236}\text{U}$ | $2.342 \times 10^7$ | 4.494        | 73.8          |
|                  |                     | 4.445        | 25.9          |
| $^{238}\text{U}$ | $4.468 \times 10^9$ | 4.198        | 79.0          |
|                  |                     | 4.151        | 20.9          |

The uranium concentration in the environment is well investigated. Natural uranium occurs in the Earth's crust and in seawater, at around 2.7 ppm and 3.0 ppb, respectively [13]. The following table shows the uranium concentration ranges in several natural systems, as soil, air, water and seawater. Due to the geological setting the uranium concentrations in water show large variations; even values of more than 1 mg per litre were found [16].

Table 2. Examples of the uranium concentration in different matrix materials

| Matrix   | Concentration                                               | Ref. |
|----------|-------------------------------------------------------------|------|
| Soil     | 0.1 – 10 mg/kg                                              | [14] |
| Air      | $8.1 \times 10^{-9} - 8.1 \times 10^{-7}$ mg/m <sup>3</sup> | [15] |
| Water    | 0.01 – 1 500 µg/l                                           | [16] |
| Seawater | ~ 3 µg/l                                                    | [17] |

The geochemistry of aqueous actinides is well known. Uranium complexes are found in surface and near-surface waters with hydroxide and carbonate as the main complex forming agents. Under oxidizing conditions aqueous uranium occurs in the hexavalent state (+VI) and under oxygen free conditions the common valence state is (+IV). It is assumed that under most environmental conditions for actinides (An) the following organic complexes can be formed:  $An(OH)_4$ ,  $An(OH)_5^-$  for An(IV) and  $AnO_2(CO_3)_2^{2-}$  and  $AnO_2(CO_3)_3^{4-}$  for An(VI) [18]. Due to an excess of  $^{234}U$  the activity ratio of  $^{234}U/^{238}U$  in water is often higher than one. This arises from preferential leaching of  $^{234}U$  from the soil/rock matrix: the recoil of the alpha decay ( $\sim 10^5$  eV) dislocates the  $^{234}U$  atom from the lattice, which increases its mobility [19]. As a consequence chemical weathering and the water/rock interactions will lead both to uranium dissolution in the aqueous phase and to  $^{234}U/^{238}U$  disequilibrium. The  $^{234}U/^{238}U$  activity ratio measured in water can give information for the explanation of hydrological, geochemical and chemical processes. According to Steier et al. [20] no fractionation of  $^{236}U/U$  can be expected because for the  $^{235}U(n,\gamma)^{236}U$  reaction the recoil energy of  $^{236}U$  is typically lower than 1 eV, which is below the displacement energy of most minerals. Uranium is an important raw material for nuclear energy production because  $^{235}U$  undergoes fission via thermal neutrons. Due to that, large amounts of power can be generated but also other important actinide elements can be synthesized, as e.g.  $^{239}Pu$  (1).



## 1.2 $^{236}\text{U}$

$^{236}\text{U}$  with a half life of  $2.342 \times 10^7$  years is produced via thermal neutron capture on  $^{235}\text{U}$ . The cross section  $\{\sigma[^{235}\text{U}(n,\gamma)] = 98 \text{ barn}\}$  is about one-sixth of the fission cross section  $\{\sigma[^{235}\text{U}(n,f)] = 583 \text{ barn}\}$ . Natural production results from neutrons present from  $(\alpha,n)$  reactions on lighter nuclides, spontaneous fission of  $^{238}\text{U}$ , induced fission of  $^{235}\text{U}$  and at the earth's surface and subsurface from cosmic rays [21]. In the 1970s naturally occurring  $^{236}\text{U}$  was found in lunar samples [22] which were measured by conventional tandem mass spectrometry. Later this research group discovered an airborne  $^{236}\text{U}$  contamination in the laboratory which has affected the already published results [23]. The first detection of natural  $^{236}\text{U}$  in uranium ore samples from Cigar Lake, (Saskatchewan, Canada) by using tandem AMS was published by Zhao et al. [24].

**Table 3.** Comparison between natural and anthropogenic  $^{236}\text{U}/^{238}\text{U}$  isotopic ratios

| Natural source                                  | $^{236}\text{U}/^{238}\text{U}$                        | Ref.                   | Anthrop. source                 | $^{236}\text{U}/^{238}\text{U}$                        | Ref.          |
|-------------------------------------------------|--------------------------------------------------------|------------------------|---------------------------------|--------------------------------------------------------|---------------|
| Uranium ores                                    | $10^{-12} - 10^{-9}$                                   | [25],<br>[26],<br>[27] | Nuclear fuel                    | up to $10^{-2}$                                        | [28]          |
| Typical rocks with a U content of several mg/kg | $1 \times 10^{-14} - 5 \times 10^{-14}$<br>(estimated) | [20]                   | Close to Chernobyl              | up to $10^{-3}$                                        | [29]          |
| Land surface                                    | $3 \times 10^{-14}$<br>(estimated)                     | [20]                   | Global Fallout                  | $10^{-8} - 10^{-7}$<br>$10^8$ $^{236}\text{U}$ atoms/g | [32]          |
| Oceans                                          | $1 \times 10^{-14} - 1 \times 10^{-13}$<br>(estimated) | [20]                   | Reprocessing plant (Sellafield) | $10^{-5} - 10^{-6}$                                    | [13],<br>[33] |

Up to now  $^{236}\text{U}/^{238}\text{U}$  isotopic ratios were measured in several uranium ores and presented in [20], [25] - [27]; the obtained ratios ranged from  $10^{-12}$  to  $10^{-9}$  (see Table 3). The latter, rather high, value was found in the Oklo deposit from one of the natural fission reactors in Gabon. For typical crustal rocks with a uranium and thorium content of several ppm ratios between  $1 \times 10^{-14}$  and  $5 \times 10^{-14}$  are expected [20]. For the land surface a ratio of about  $3 \times 10^{-14}$  is estimated and for the oceans it should be in the range of  $10^{-14}$  to  $10^{-13}$  [20]. All these values are based on estimations and up to the present no research group was able to detect such low isotopic ratios. It was not a question of an appropriate AMS facility but rather to find and

separate a respective sample and to reduce the possible anthropogenic input during the sample treatment (e.g. cross-contamination).

Today much more anthropogenic  $^{236}\text{U}$  exists as it is produced as a by-product in nuclear reactors. Significant releases to the environment can be expected, but the environmental distribution of anthropogenic  $^{236}\text{U}$  is not well investigated yet. For nuclear fuel ratios up to  $10^{-2}$  were obtained and in soils from the vicinity of the Chernobyl power plant ratios up to  $10^{-3}$  were found [28], [29]. Until now the environmental  $^{236}\text{U}$  studies were focused on anthropogenically affected sites: Beasley et al. [30] reported isotopic measurements in soils contaminated due to the accident at Mayak (1957) and soil samples at/near the Semipalatinsk-21 site. A sediment core from the Esk Estuary, West Cumbria (UK) which is ca. 5 km south of the marine effluent discharge from BNFL Sellafield was analysed for the respective  $^{236}\text{U}/^{238}\text{U}$  ratio in each layer [13]. Ketterer et al. [14] determined elevated  $^{236}\text{U}/^{238}\text{U}$  isotopic ratios in soil samples near the Rocky Flats Environmental Technology site and sediment samples. In the 30 km relocation area around Chernobyl soils were investigated using  $^{236}\text{U}$  as the tracer of irradiated reactor uranium [29] and the same was done also up to a distance of 200 km from Chernobyl [8]. Recently river sediments near the Gargliano nuclear power plant were investigated by Quinto et al. [31]. Soil samples which were solely influenced by global fallout have shown an  $^{236}\text{U}/^{238}\text{U}$  isotopic ratio of  $10^{-8}$  to  $10^{-7}$ . However, according to Sakaguchi et al. [32], the more meaningful number is probably the  $^{236}\text{U}$  concentration [atoms/g], as it might be possible that the ratio changed by different leaching efficiencies of natural  $^{238}\text{U}$  from the soil matrix; the obtained value was  $10^8$   $^{236}\text{U}$  atoms/g.

The huge difference of several orders of magnitude between the natural and anthropogenic  $^{236}\text{U}/^{238}\text{U}$  atom ratios offers great potential in tracing releases of reactor-irradiated U in environmental samples containing also natural U. The mixing of reactor-irradiated U with natural U causes, even if only small amounts of  $^{236}\text{U}$  are present, a greatly elevated  $^{236}\text{U}/^{238}\text{U}$  atom ratio compared to the background, and so large mixing ratios can be observed [14].

In conclusion, if the isotopic ratio of  $^{236}\text{U}/^{238}\text{U}$  is higher or equal  $10^{-9}$ , an anthropogenic contribution can be assumed. Possible anthropogenic contributions can be local leakage from nuclear facilities, widespread contamination from Chernobyl or global fallout from the atmospheric nuclear weapon tests during the 1950s and early 1960s.

During this work both naturally and anthropogenically occurring  $^{236}\text{U}$  was investigated to get a first impression about the spreading of  $^{236}\text{U}$ .

### 1.3 Plutonium and Americium

#### Plutonium

Pu is the 6<sup>th</sup> member of the actinide group with the electronic configuration  $[\text{Rn}]5f^67s^2$  and it can exist in aqueous solution in the oxidation states 3+ to 6+. Pu can co-exist in different oxidation states simultaneously and can be transferred easily to a given oxidation state by changing the redox conditions [34]. All Pu isotopes are radioactive and the isotopes of most concern as environmental contaminants are presented in Table 4.

Small amounts of naturally produced Pu can be found in nature. Seaborg and Perlman were the first who isolated traces of  $^{239}\text{Pu}$  in 400 g pitchblende from the Great Bear Lake region of Canada [35].

**Table 4.** Nuclear properties of Pu isotopes

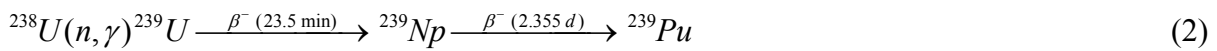
| Isotope           | Half life [a]       | Energy [MeV]            | Abundance [%] |
|-------------------|---------------------|-------------------------|---------------|
| $^{238}\text{Pu}$ | 87.74               | 5.499                   | 70.91         |
|                   |                     | 5.456                   | 28.98         |
| $^{239}\text{Pu}$ | $2.411 \times 10^4$ | 5.157                   | 73.3          |
|                   |                     | 5.144                   | 15.1          |
| $^{240}\text{Pu}$ | 6563                | 5.168                   | 72.8          |
|                   |                     | 5.124                   | 27.1          |
| $^{241}\text{Pu}$ | 14.35               | 20.82 keV ( $\beta^-$ ) | 100           |
| $^{242}\text{Pu}$ | $3.750 \times 10^5$ | 4.901                   | 77.5          |
|                   |                     | 4.856                   | 22.4          |

Plutonium and americium of anthropogenic origin can be found in the environment because of nuclear weapons testing (e.g. Marshall Islands, Mururoa, Semipalatinsk), nuclear reactor accidents (Chernobyl, Windscale), discharges of radioactive waste (Sellafield, La Hague, Mayak) and accidents with nuclear devices (e.g. Palomares, Thule) [36]. Elevated levels of these elements indicate an anthropogenic contamination. It is well investigated that Pu isotopic ratios vary with reactor type, nuclear fuel burn-up, neutron flux and energy. For fallout from nuclear detonations the ratio depends on the weapon type and also on the yield as 100% efficiency is not possible in a nuclear explosion [37]. The Pu isotopic signature provides good information on the Pu origin. Some examples are presented in Table 5 (see Oughton et al. [38] and references therein).

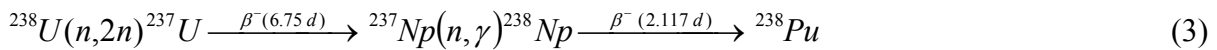
**Table 5.** Anthropogenic sources and their  $^{240}\text{Pu}/^{239}\text{Pu}$  isotopic ratios

| Source                               | $^{240}\text{Pu}/^{239}\text{Pu}$ |
|--------------------------------------|-----------------------------------|
| Global Fallout – Northern Hemisphere | 0.175 - 0.19                      |
| Chernobyl – fuel particle            | 0.45 - 0.52                       |
| Irish Sea – sediment profile         | 0.05 - 0.25                       |
| Semipalatinsk                        | $0.036 \pm 0.001$                 |
| Bikini Atoll                         | $0.338 \pm 0.051$                 |

Pu is one of the most important transuranium elements because it can be used as fuel in nuclear power plants as well as for nuclear weapons. Especially  $^{239}\text{Pu}$  with its very long half life of  $2.411 \times 10^4$  years is both fissile and can be easily produced in large amounts due to neutron bombardment of  $^{238}\text{U}$  (2).



$^{238}\text{Pu}$  can be produced with successive high-energy neutron bombardment according to the following reaction pathway (3). It can be used e.g. as energy supply for space-related satellites or pace makers [39].

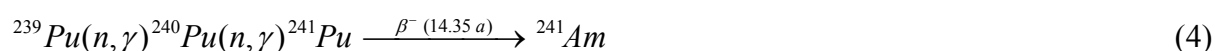


In soil samples  $^{238}\text{Pu}$ ,  $^{239}\text{Pu}$ ,  $^{240}\text{Pu}$  (all alpha emitters) and  $^{241}\text{Pu}$  (beta emitter) are the most relevant Pu isotopes. In general for the determination of Pu isotopes radioanalytical techniques like alpha spectrometry for the measurement of the alpha emitter isotopes ( $^{238}\text{Pu}$  and  $^{239(40)}\text{Pu}$ ) and liquid scintillation counting for the soft beta emitter  $^{241}\text{Pu}$  is used [40]. Unfortunately the drawback of these techniques is the long measurement time, which may take from days to weeks depending on the activity of the respective nuclide and precision required. Furthermore the isotopic ratio  $^{240}\text{Pu}/^{239}\text{Pu}$  cannot be determined by conventional alpha spectrometry due to their similar energies ( $^{239}\text{Pu}$ : 5.16 MeV, 73.3% and  $^{240}\text{Pu}$ : 5.17 MeV, 76 %) which is an important tool for the assessment of the anthropogenic origin [41]. At the beginning thermal ionization mass spectrometry (TIMS) was the primary tool to determine the Pu isotopic composition. With time, especially during the last decade,

inductively coupled plasma mass spectrometry (ICP-MS) has become the preferred alternative. Resonance ionization mass spectrometry (RIMS) and accelerator mass spectrometry (AMS) did not establish for routine measurements due to high instrumental costs and difficult operation [42].

### Americium

Americium does not occur naturally and was first synthesised in 1944 via bombardment of  $^{239}\text{Pu}$  with neutrons [43] which is shown in (4).



Americium is the 7<sup>th</sup> member of the actinide group with the electronic configuration  $[\text{Rn}]5f^7 7s^2$  and it can exist in aqueous solution in the oxidation states 3+ to 6+.  $^{241}\text{Am}$  is a long-lived radionuclide with a half life of 432.2 years and an alpha emitter (5.486 MeV, 84.5% and 5.443 MeV, 13.0%) as well as a gamma emitter (59.5 keV, 35.9%). This isotope is the decay product of  $^{241}\text{Pu}$  and is therefore the most interesting isotope in environmental samples. The reason is that the concentration of  $^{241}\text{Am}$  will increase in the environment because of its in-growth from the high activities of  $^{241}\text{Pu}$  released to nature.

Both radionuclides can be released due to nuclear weapons tests, nuclear accidents or reprocessing facilities. The determination of  $^{241}\text{Am}$  in the Bq/g range is relatively straightforward using gamma spectrometry. Lower levels of  $^{241}\text{Am}$  are measured by alpha spectrometry together with  $^{243}\text{Am}$  for the yield determination. Due to the similar behaviour of the trivalent lanthanides and Am(III), they can interfere the alpha spectrometry measurement. Therefore one has to consider this contribution especially for soil samples [44].

## 1.4 Analytical methods

For the analysis of uranium and transuranium radionuclides first several sample preparation steps, like pre-concentration, co-precipitation, solvent extraction, ion exchange or extraction chromatographic steps have to be carried out. Afterwards they can be measured by relatively cheap radioanalytical techniques, such as alpha spectrometry and liquid scintillation spectrometry [34].

The purpose of sample pre-treatment is basically the same for all investigated actinides: to obtain a homogeneous sample solution which contains the analyte without significant losses, free of any insoluble residues which might interfere during the subsequent chemical procedure or retain the analyte as well as free of any organic material that could form complexes with the analyte or reagents [45].

Pre-concentration by evaporation is useful for the determination of actinides because of their ultralow concentration in the environment. The drawback of this method is that not only the actinide concentration increases but also the amount of other matrix elements which could cause interferences during the column chromatography steps. To avoid this problem a co-precipitation (e.g. with  $\text{Fe}(\text{OH})_3$ ,  $\text{Ca}_3(\text{PO}_4)_2$ ,  $\text{CaF}_2$ ) can be carried out to remove the major anions [46].

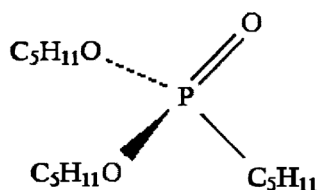
Large soil or sediment samples ( $> 10$  g) or water samples ( $> 5$  L) are necessary for the determination of low-level actinides analysis. As U occurs naturally in the ppm range in soils, it can be determined without problems in smaller sample sizes. But if larger amounts of sample material are reprocessed, the chemical recoveries are variable because of interferences from major ions, the so called “matrix effects” [47]. Acid decomposition is a common method for nearly all sample matrices and as actinides are soluble in  $\text{HNO}_3$  and  $\text{HCl}$  most of the procedures for the decomposition of actinide containing samples are based on these acids [5].

For the column separation step various ion exchange resins (as e.g. Dowex 1) can be used. Ion exchange resins are high-molecular organic compounds based on e.g. styrene copolymerized with divinylbenzene (DVB) containing different functional groups covalently bound to the polymer [34]. For cation exchangers, e.g.  $-\text{SO}_3\text{H}$ ,  $-\text{COOH}$ ,  $-\text{OH}$ ,  $-\text{SH}$  or for anion resins e.g.  $-\text{NH}_2$ ,  $-\text{NHR}$  ( $\text{R}$  = alkyl group),  $-\text{NR}_2$ ,  $-\text{NR}_3^+$  are used. The ion exchange process is based on the replacement of the exchangeable ion from the resin by analogously charged ions. The selectivity, i.e. the extent to which one ion is preferentially absorbed compared to another ion, determines the efficiency of the separation and the readiness with which two or more ions with the same charge can be separated [48]. In this work Dowex 1x2 (for U and Pu) and Dowex 1x8 (for Pu) was used. The Dowex resins consist of styrene and DVB co-polymers. Dowex 1x2 means Dowex 1 with 2 % DVB used in the polymerisation step. The U separation using Dowex 1x2 in 8M  $\text{HCl}$  and elution with 0.1M  $\text{HCl}$  [49] was a commonly used method in our laboratory for 1 - 2.5 L water samples but it had not turned out satisfactory for larger surface and well water samples (5 L and more). The problem seemed to be the huge calcium content after the pre-concentration which often blocked the column. Later on U was separated

from the water samples with UTEVA<sup>®</sup> resin according to a procedure given by Eichrom Technologies, Inc. [50].

The Dowex 1x2 method was applied for soil samples (La Palma) too, but as these samples contained a huge amount of iron which interfered with the U determination because large quantities of co-adsorbed Fe can partly or completely prevent the U adsorption. The reason is that its anionic chloride complex may replace that of U on the resin [48]. Also for this work the UTEVA<sup>®</sup> resin and the Eichrom Technologies, Inc. procedure [51] was used. Here most of the Fe could be removed before the U elution started.

For the Pu separation both resins (Dowex 1x2 and Dowex 1x8) can be used without problems. Dowex 1 is a strong basic anion exchanger and Pu(IV) and Pu(VI) are strongly retained from higher concentrated HNO<sub>3</sub> and HCl. A convenient way to separate Pu selectively from other actinides or e.g. from Fe is, to load Pu(IV) in 8M HNO<sub>3</sub> on the anion resin. This step is the same for both (Dowex 1x2 and Dowex 1x8) resins. But the elution steps are different; in the case of Dowex 1x2 the elution solution was 0.36M HCl – 0.014M HF [52] and for the other one 0.1M NH<sub>4</sub>I – 9M HCl [53] was used. Of course the advantage of the latter method is that no HF is necessary and therefore no Teflon beaker is used which means that the evaporation process on the hotplate is much faster; not to mention the safety risks when working with HF. The UTEVA<sup>®</sup> resin is based on extraction chromatography which is a well suited method for the separation of radionuclides from a wide range of sample matrices. UTEVA<sup>®</sup> resin is a special resin for uranium and tetravalent actinides with dipentyl pentylphosphonate (DP[PP]) as the stationary phase (see Figure 2). The UTEVA<sup>®</sup> resin extracts tetra- and hexavalent actinides from HNO<sub>3</sub> solution of high concentration (> 1 mol/l) simultaneously and only small amounts of stripping solution are needed [54].



**Figure 2.** Dipentyl pentylphosphonate (DP[PP])

The extraction chromatography consists of three components, namely the inert support, the stationary phase and the mobile phase. The separation of the sample ions is based on the distribution of the respective cations between an organic and an aqueous phase (neutral or acidic). The ions of interest are adsorbed on the surface of an inert support and acts as the

stationary phase. In the meantime, especially after UTEVA<sup>®</sup>, TEVA<sup>®</sup>, TRU<sup>®</sup>, etc. became commercially available, extraction chromatography is generally used for the separation of radionuclides.

Alpha spectrometry is a commonly used measurement technique but the disadvantage of the chemical separation is that several purification steps are necessary which are time-consuming, and often long counting times are necessary, especial for Pu in environmental samples. For the source preparation for alpha spectrometry three methods are well known: evaporation, micro-precipitation with a rare-earth fluoride and electrodeposition [45]. For the evaporation method the sample solution is deposited onto a stainless steel or platinum disk and evaporated carefully to obtain a uniformly covered layer. By using electrodeposition, the actinides are electrochemically plated from an electrolyte solution on a stainless steel or platinum disk [34]. The technique is time-consuming and is affected by current fluctuations and pH changes during the electrodeposition [55]. This technique gave way to the micro-precipitation which is carried out with NdF<sub>3</sub> or CeF<sub>3</sub> [55], [56]. The solution containing the precipitation is filtered through a cellulose nitrate membrane filter (Whatman<sup>®</sup>, 0.1 µm pore size) and the advantage of this type of filter is that one can dissolve it very easily in HNO<sub>3</sub> and H<sub>2</sub>O<sub>2</sub> [52]. This is necessary if the samples should be reprocessed for an AMS measurement [57].

## 1.5 Applied measurement techniques

In this subsection only the measurement techniques used during this work were described. That was mainly alpha spectrometry and Accelerator Mass Spectrometry (AMS). The first method was used for the yield determination of U and Pu and for the U concentration and <sup>239(40)Pu</sup> activity, respectively. Liquid Scintillation Counting (LSC) was only applied for artificial uranium solutions testing the extraction and re-extraction from U by ionic liquids. This technique was chosen as a quick check whether our experiments are working and therefore carrying out a micro-precipitation and measuring these samples by alpha spectrometry would have been too time-consuming. Finally, AMS is described because all samples, except the samples with the ionic liquid application, were either measured for their <sup>236</sup>U/<sup>238</sup>U isotopic ratios or for their <sup>240</sup>Pu/<sup>239</sup>Pu ratios and for a few also the <sup>241</sup>Am/<sup>243</sup>Am ratio was determined.

### 1.5.1 Alpha spectrometry

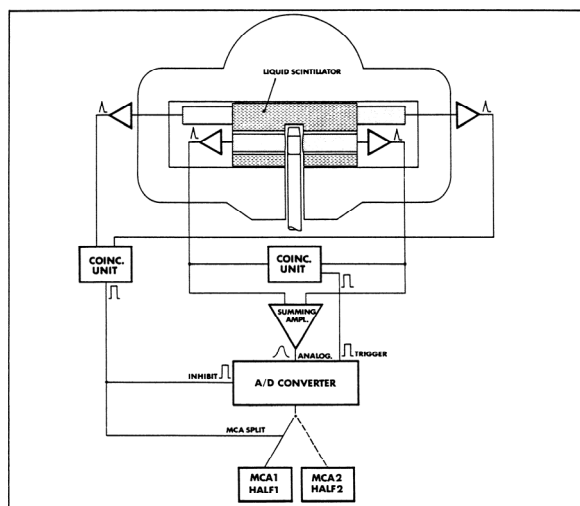
Alpha spectrometry is most frequently performed using silicon surface-barrier detectors. The measurement is conducted at room temperature in a vacuum chamber to avoid energy losses and peak broadening. The alpha particles emitted from the sample source are stopped within a thin surface area of the detector. The number of resulting electron-hole pairs is directly proportional to the alpha energy of the particles [58]. The main advantage of this technique is the relatively low price of the equipment, the high sensitivity because of the low background and the high selectivity for alpha particles against other types of radiation [34].

Due to the short path length of alpha particles in solid state matter the source should be very thin (a few  $\mu\text{m}$ ) to avoid losses due to self-absorption. Therefore the minor and major matrix components have to be removed by chemical separation. If this is not done the alpha spectra become degraded and the peak resolution is diminished which can, in the worst case, prevent an evaluation of the spectra [34]. As the alpha energies of  $^{239}\text{Pu}$  and  $^{240}\text{Pu}$  are quite similar ( $^{239}\text{Pu}$ : 5.16 MeV, 73.3% and  $^{240}\text{Pu}$ : 5.17 MeV, 76 %) the ratio  $^{240}\text{Pu}/^{239}\text{Pu}$ , which is a very important tool to identify the origin of the plutonium, cannot be determined. Beside the often time-consuming chemical separation steps, the long measurement times for the determination of environmental samples with low e.g. Pu activity is another disadvantage [59]. During this work alpha spectrometry was used for the chemical yield determination of the sample procedure, as well as for the measurement of the  $^{238}\text{U}$ ,  $^{234}\text{U}$  and  $^{239(40)}\text{Pu}$  activity concentrations. In general the counting time for the investigated samples were 252 000 s but for the Pu samples from La Palma the time had to be prolonged to 604 800 s.

### 1.5.2 Liquid Scintillation Counting (LSC)

LSC has been a very popular technique for the detection and quantitative measurement of low level radionuclides since the early 1950s [60]. Low levels of detection can be achieved by using passive and active shields. The passive shielding consists of an asymmetrical lead shield with the largest diameter on the top of the measuring position to suppress the cosmic radiation. The second inner layer is cadmium to absorb low energy and thermal neutrons. Additionally, this layer absorbs lead X-rays which are produced by photoelectric effect reactions. The inner part of the passive shield is the copper container of the active liquid scintillation guard. For background event detection two photomultiplier (PM) tubes are used

and again two PMs for coincident sample counting. Any signal observed within the guard detectors simultaneously with the sample detectors is not accepted as a sample event as the sample detectors are operated in anticoincidence with the guard detectors [61]. A schematic diagram of the Quantulus 1220 circuit is shown in Figure 3.



**Figure 3.** Schematic diagram of the Quantulus 1220 low-level liquid scintillation counter (Wallac Oy<sup>®</sup>, Finland, now Perkin Elmer<sup>®</sup>) [61].

The principle of LSC can be briefly summarized as follows: the radioactive sample solution is mixed with an organic liquid scintillator. After mixing the solution should be homogeneous and colourless because otherwise an intensity loss due to quenching results. The activator molecules transform the decay energy into excited states and by returning to the ground state photons were emitted. At the photocathode of the photomultiplier tube the photons are releasing electrons which in turn are multiplied by the dynodes of the multiplier to give pulses of several mV [58], [60].

LSC is in principle a rapid, simple and routine analytical method for many radionuclides, e.g.  $^{241}\text{Pu}$  [62],  $^{90}\text{Sr}$  [63],  $^{222}\text{Rn}$ ,  $^{228}\text{Ra}$ ,  $^{226}\text{Ra}$ ,  $^{210}\text{Pb}$ ,  $^{210}\text{Po}$  [64]. Originally developed for measuring low-energy betas, pulse-shape analysis enables also the measurement of alpha emitters. During this work LSC was used as a rapid test method to monitor the U concentration after extraction from the aqueous phase with the respective ionic liquid (IL) and again after re-extraction from the IL.

### 1.5.3 Accelerator Mass Spectrometry (AMS)

Among the various methods of mass spectrometry (e.g. ICP-MS, TIMS, RIMS, etc.), Accelerator Mass Spectrometry (AMS) is the most sensitive method to measure isotope ratios between  $10^{-10}$  and  $10^{-16}$  [65] or small amounts ( $10^5$  to  $10^8$  atoms per sample) [66]. As the radioactive atoms are detected directly and not by their radioactive decay, the measuring times and sample sizes are reduced by many orders of magnitude compared to conventional decay counting. The most familiar example for the applicability of AMS is the measurement of radiocarbon ( $^{14}\text{C}$ ) for archaeological purposes. The possibility of ultra low level determination of long-lived radionuclides was also realised by AMS. Due to the high sensitivity it enables the measurement of activity levels well below those detectable by routine radiochemical methods, e.g. for  $^{236}\text{U}$  as well as for  $^{239}\text{Pu}$  and  $^{240}\text{Pu}$  which cannot be resolved by conventional alpha spectrometry due to their similar alpha energies. Fifield described in [67] the principles of AMS with the emphasis on the  $^{239,240}\text{Pu}$  and  $^{236}\text{U}$  measurement.

Typical measurement conditions at the VERA facility for  $^{236}\text{U}$  and  $^{239}\text{Pu}$  are summarized in Table 6. Compared with alpha spectrometry AMS has low matrix and interference effects but, on the other hand, AMS measurements are more complex and a well experienced team is required. An advantage of this technique is that it gives information about atomic ratios like  $^{240}\text{Pu}/^{239}\text{Pu}$  which identify anthropogenic sources of Pu.

The detection limits of  $^{236}\text{U}/^{238}\text{U}$  with conventional mass spectrometry are  $\sim 10^{-10}$  [25]. Therefore the determination of natural  $^{236}\text{U}$  is difficult and at this ultra-trace levels only possible at very few specialized AMS facilities [65], [68]. At the moment only two AMS facilities are aiming for the natural isotopic ratio of  $^{236}\text{U}/^{238}\text{U}$  below  $10^{-10}$ . One laboratory is in Canberra (Australia) and the other is VERA in Vienna (Austria). The sensitivity limits for alpha spectrometry, AMS, TIMS, ICP-MS and RIMS are summarized in [69] and references therein.

**Table 6.** Parameters for  $^{236}\text{U}$  and  $^{239}\text{Pu}$  measured at VERA, modified from [70].

| Trace isotope                                                | $^{236}\text{U}$                                   | $^{239}\text{Pu}$                                        |
|--------------------------------------------------------------|----------------------------------------------------|----------------------------------------------------------|
| Target material                                              | $\text{Fe}_2\text{O}_3$                            | $\text{Fe}_2\text{O}_3$                                  |
| Injection energy                                             | 56 keV                                             | 56 keV                                                   |
| Injected ion                                                 | $^{236}\text{U}^{16}\text{O}^-$                    | $^{239}\text{Pu}^{16}\text{O}^-$                         |
| Terminal voltage                                             | 3.0 MeV                                            | 3.0 MeV                                                  |
| Analyzed ion <sup>1</sup>                                    | $^{236}\text{U}^{5+}$                              | $^{239}\text{Pu}^{5+}$                                   |
| Reference ion <sup>2</sup>                                   | $^{238}\text{U}^{5+}$                              | $^{242}\text{Pu}^{5+}$ (spike) or $^{239}\text{Pu}^{5+}$ |
| Typ. neg. ion current <sup>3</sup><br>(of reference species) | 50 - 100 nA<br>( $^{238}\text{U}^{16}\text{O}^-$ ) | $^{239}\text{Pu}$ : < 5 cps                              |
| Stripping yield <sup>4</sup>                                 | 5%                                                 | ca. 5%                                                   |
| Machine background <sup>5</sup>                              | $\ll 2 \times 10^{-12}$                            | ~ 1 count per hour                                       |
| Detector efficiency <sup>6</sup>                             | 20%                                                | 20%                                                      |
| Total efficiency <sup>7</sup>                                | $10^{-4}$                                          | $10^{-4}$                                                |
| Typ. Precision <sup>8</sup>                                  | < 5%                                               | < 5%                                                     |

<sup>1</sup> In the case of  $^{240}\text{Pu}$ : sometimes  $^{240}\text{Pu}^{7+}$ .

<sup>2</sup> For Pu no current is available, only count rate.

<sup>3</sup> For  $^{242}\text{Pu}$  spike: 10-100 cps, for  $^{239}\text{Pu}$  in Irish Sea sediments: ~ 300 cps, for  $^{239}\text{Pu}$  in La Palma soils: < 1cps cps...counts per second

<sup>4</sup> Ratio of analysed reference ion to injected ion, including ion optical losses.

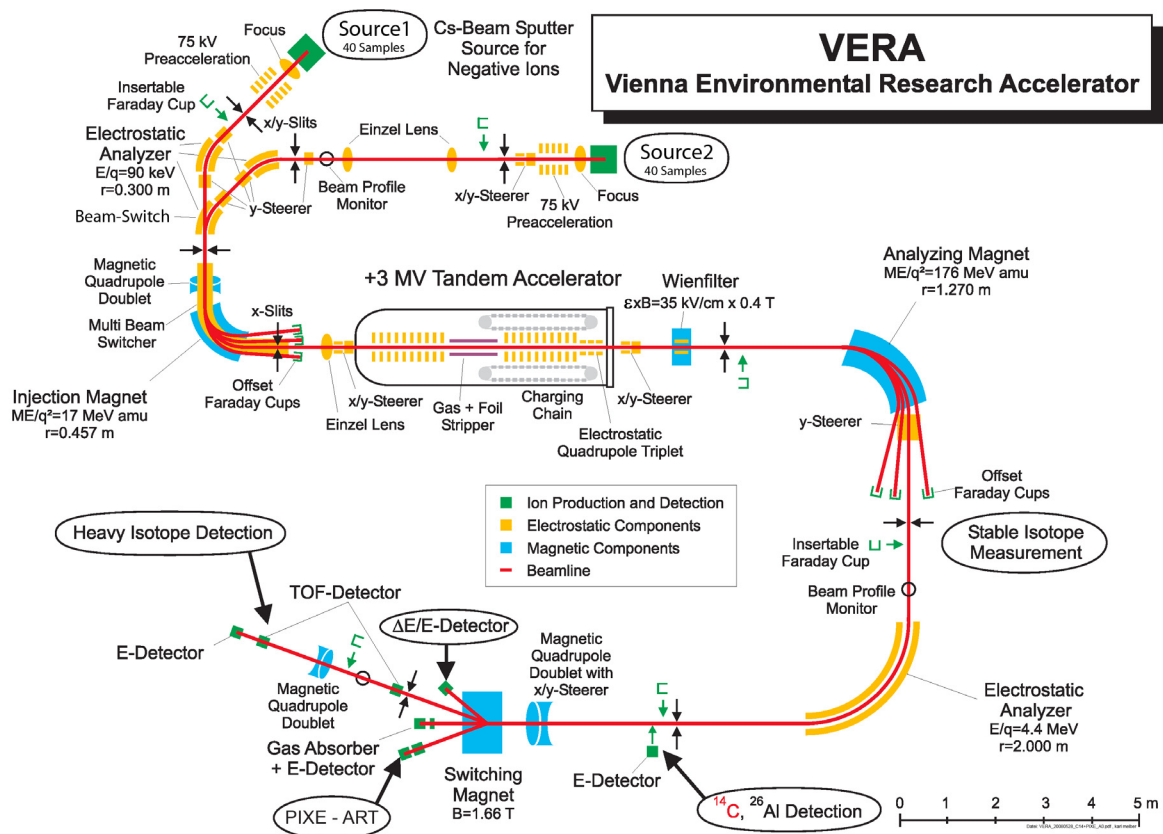
<sup>5</sup> Quoted for the ratio of trace to reference isotope; the chemistry blank will be higher.  
For Pu: probably from the ion source.

<sup>6</sup> Measured as the fraction of analysed ions observed in the final detector.

<sup>7</sup> Measured as counts in detector per total number of atoms in the sputter target.

<sup>8</sup> For the ratio of trace to reference isotope in a sample significantly above the background and the efficiency limit.

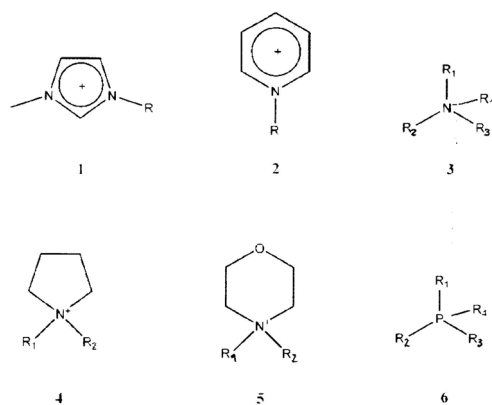
In Figure 4 the most recent scheme of the VERA facility is shown. Forty sputter targets can be mounted in one sample wheel. The basic principle can be summarized as follows: negative ions were extracted from a caesium sputter source and mass selected with an electrostatic analyser (ESA) and an injection magnet. Afterwards the ions are injected into the accelerator with a terminal voltage of 3 MV and pass the gas stripper (Ar, now O<sub>2</sub>) where they lose their electrons. At this step also molecular isobars were removed (mainly <sup>235</sup>UOH<sup>-</sup> for <sup>236</sup>UO<sup>-</sup> and <sup>238</sup>UOH<sup>-</sup> for <sup>239</sup>PuO<sup>-</sup>). The positively charged ions (e.g. U<sup>5+</sup> and Pu<sup>5+</sup>) were accelerated to 18 MeV and after another mass analysis the ion species of interest is identified in a Time-of-Flight (TOF) and energy detector [69],[71].



**Figure 4.** The upgraded schematic layout of the VERA facility [70].

## 1.6 Ionic liquids

Ionic liquids (ILs) are composed of fully dissociated ions and are of growing interest in the field of green chemistry, as they are not flammable, have a negligible volatility, a wide liquid temperature range, high thermal stability, water immiscibility, electrical conductivity and tuneable physical properties [72]. They are used as solvents in chemical processes for replacing volatile organic compounds (VOCs), in the nuclear industry for the reprocessing of irradiated nuclear fuel [73], and for the understanding of interactions of biomolecules with uranium species [74]. Often large organic cations are used as positive ions for ILs. In Figure 5 commonly used cations are shown; (1) indicates 1-alkyl-3-methylimidazolium, (2) 1-alkylpyridinium, (3) quaternary ammonium, (4) 1,1'-dialkylpyrrolidinium, (5) 1,1'-dialkylmorpholinium and (6) phosphonium.



**Figure 5.** Commonly used cations in ILs [75].

Nowadays ILs are increasingly important for liquid/liquid extraction of metal ions like uranium from the nuclear power plant waste stream [76].

As the conventional anion exchange step for uranium separation is very time-consuming for large water samples (25 L and more) the investigation of ionic liquids (ILs) for uranium extraction was carried out during this work. First different ILs were tested for their extraction capability on artificial uranium solutions. After selecting the best suited one the U was extracted from a real water matrix and the removal of Ca was investigated.

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## 2. Main tasks of this thesis

- (1) To develop the sample preparation with regard to the measurement of  $^{236}\text{U}$  in environmental samples by AMS.
- (2) To measure and study  $^{236}\text{U}$  in different natural materials such as yellow cake, uranium ore, water, soil and sediment samples.
- (3) To test the feasibility of ionic liquids for the extraction of uranium from aqueous solutions.

### Novelty and importance of this thesis

Measurements in various natural compartments are carried out to get an overview of the anthropogenic distribution of  $^{236}\text{U}$  in the environment. This is a prerequisite for further geological, hydrological and environmental studies.

For better explanation of the anthropogenic source also Pu was investigated in soil and sediment samples.

The thesis is structured as follows: first natural materials (yellow cake and uranium ore samples) were investigated for their  $^{236}\text{U}/^{238}\text{U}$  ratios, then water and soil samples from non-contaminated sites and finally sediment samples from the Irish Sea. The analysis of these different sample types was focused on  $^{236}\text{U}$  but in the soil and sediment samples additionally Pu was measured. Furthermore investigations were carried out with ionic liquids to simplify the chemical treatment for large water samples.

In Chapter 3.1 the feasibility of using the  $^{236}\text{U}/^{238}\text{U}$  isotopic ratio to reconstruct the origin by comparing four pairs of uranium ores with yellow cake samples is investigated. Four pairs are a very small sample number and the analysis of only one uranium ore sample from a large deposit is not representative enough. Due to these facts it was concluded that the usage of yellow cake as starting material for fingerprinting of natural uranium could be more successful because typically, several tons of ore are used to produce a batch of yellow cake. Therefore problems emerging from ore in-homogeneities should be eliminated.

Supplementary investigations of pre-nuclear materials (i.e. material which is free of anthropogenic  $^{236}\text{U}$  from global fallout or Chernobyl) are discussed in Chapter 3.1.1. The samples were analysed and measured to verify whether they were irradiated in the past. These two studies represent the natural part of  $^{236}\text{U}$ .

In Chapter 3.2 and Chapter 3.3 environmental samples from remote clean sites were investigated. Chapter 3.2 gives an overview about the isotopic ratio  $^{236}\text{U}/^{238}\text{U}$  in natural water samples (i.e. river, creek and well water) with the emphasis on the Austrian region. In Chapter 3.2.1 supplemental measurements of further Austrian water samples and some Slovakian and Slovenian waters were presented. Due to the obtained results an anthropogenic influence from global fallout and/or Chernobyl can be assumed. A definitive source identification was not possible as no other radioisotopes were investigated.

Chapter 3.3 describes the determination of U and Pu in soil samples from La Palma with the emphasis on the vertical distribution of  $^{236}\text{U}/^{238}\text{U}$  at three locations. The  $^{240}\text{Pu}/^{239}\text{Pu}$  ratio was measured to assess the source of contamination: it showed a global fallout signature. This result could be confirmed by the  $^{236}\text{U}/^{239}\text{Pu}$  isotopic ratio. Supplementary investigations were carried out on soil samples from New Zealand (Chapter 3.3.1). Also here U and Pu were measured and the obtained  $^{240}\text{Pu}/^{239}\text{Pu}$  ratios confirmed the global fallout signature.

The analysis of anthropogenic samples, namely Irish Sea sediments, is presented in Chapter 3.4. The  $^{236}\text{U}/^{238}\text{U}$  results were far above the natural background and the  $^{240}\text{Pu}/^{239}\text{Pu}$  ratios agreed very well with the values already measured in this area. Furthermore the  $^{241}\text{Am}/^{243}\text{Am}$  ratio was measured for the first time by AMS and compared with alpha spectrometry results.

In Chapter 3.5 the analytical task of using ionic liquids (ILs) for the extraction of U from aqueous solution and the stripping of U from the respective ILs is demonstrated. First artificial U solutions were used for extraction experiments and finally the best suited IL was tested to extract U from a real water matrix; further on the conditions for efficient uranium back extraction were elucidated.

All in all this study presents the investigation of various sample types for their  $^{236}\text{U}/^{238}\text{U}$  isotopic ratios. Due to the  $^{240}\text{Pu}/^{239}\text{Pu}$  ratio in the soil samples an identification of the anthropogenic source was possible. The chosen sample materials give an overview about the naturally and anthropogenically occurring  $^{236}\text{U}$  in our environment.

### 3. Results

During my doctoral thesis different sources of  $^{236}\text{U}$  were investigated and the presented results are based on following publication:

#### **Investigation of the $^{236}\text{U}/^{238}\text{U}$ isotope abundance ratio in uranium ores and yellow cake samples**

M. Srncik, K. Mayer, E. Hrnccek, M. Wallenius, Z. Varga, P. Steier, G. Wallner  
Radiochim. Acta, revised manuscript submitted (Jan. 2011).

M.S. prepared the samples; E.H. helped with sample choice; P.S. performed the AMS measurements; M.S. wrote the manuscript; K.M. and P.S. assisted in writing the article; M.W., Z.V and G.W assisted in reviewing the article and helpful discussions.

Contribution of M.S. to the article: 60%.

#### **Determination of the isotopic ratio $^{236}\text{U}/^{238}\text{U}$ in Austrian water samples**

M. Srncik, P. Steier, G. Wallner

Nucl. Instrum. Meth. B **268** (2010) 1146-1149.

M.S. prepared the samples; P.S. performed the AMS measurements; M.S. wrote the manuscript; P.S. assisted in data interpretation; P.S. and G.W assisted in reviewing the article and helpful discussions.

Contribution of M.S. to the article: 75%.

#### **Depth profile of $^{236}\text{U}/^{238}\text{U}$ in soil samples in La Palma, Canary Islands**

M. Srncik, P. Steier, G. Wallner

J. Environ. Radioact., revised manuscript submitted (Jan. 2011).

M.S. prepared the samples; P.S. performed the AMS measurements; M.S. wrote the manuscript; P.S. and G.W assisted in reviewing the article and helpful discussions.

Contribution of M.S. to the article: 75%.

**Determination of U, Pu and Am isotopes in Irish Sea sediment by a combination of AMS and radiometric methods**

M. Srncik, E. Hrnccek, P. Steier, G. Wallner

J. Environ. Radioact., manuscript accepted for publication.

DOI information: 10.1016/j.jenvrad.2011.01.004

M.S. prepared the samples; P.S. performed the AMS measurements; M.S. wrote the manuscript; E.H. and P.S. assisted with data interpretation; G.W assisted in reviewing the article and helpful discussions.

Contribution of M.S. to the article: 60%.

**Uranium extraction from aqueous solutions by ionic liquids**

M. Srncik, D. Kogelnig, A. Stojanovic, W. Körner, R. Krachler, G. Wallner

Appl. Radiat. Isotopes **67** (2009) 2146-2149.

G.W. conceived the initial idea; D.K. prepared and characterized the ILs; M.S. and D.K. conducted liquid-liquid extraction experiments; M.S. carried out LSC measurements; A.S. measured ICP-OES under the assistance of W. K.; M. S., D. K. and A. S. wrote the article; G.W. and R K. assisted in reviewing the article and with helpful discussions.

Contribution of M.S. to the article: 40%

Furthermore I contributed within the scope of this thesis to the following manuscripts and publications:

**Natural and anthropogenic  $^{236}\text{U}$  in environmental samples**

P. Steier, M. Bichler, L. K. Fifield, R. Golser, W. Kutschera, A. Priller, F. Quinto, S. Richter, M. Srncik, P. Terrasi, L. Wacker, A. Wallner, G. Wallner, K. M. Wilcken, E. M. Wild  
Nucl. Instrum. Meth. B **266** (2008) 2246-2250.

Contribution of M.S. to the article: 20 %

**The first use of  $^{236}\text{U}$  in the general environment and near a shut down Nuclear Power Plant**

F. Quinto, P. Steier, G. Wallner, A. Wallner, M. Srncik, M. Bichler, W. Kutschera, F. Terrasi, A. Petraglia, C. Sabbarese  
Appl. Radiat. Isotopes **67** (2009) 1775-1780.

Contribution of M.S. to the article: 15 %

**Analysis and application of heavy isotopes in the environment**

P. Steier, F. Dellinger, O. Forstner, R. Golser, K. Knie, W. Kutschera, A. Priller, F. Quinto, M. Srncik, F. Terrasi, C. Vockenhuber, A. Wallner, G. Wallner, E. M. Wild  
Nucl. Instrum. Meth. B **268** (2010) 1045-1049.

Contribution of M.S. to the article: 10 %



***Investigation of the  $^{236}\text{U}/^{238}\text{U}$  isotope abundance ratio  
in uranium ores and yellow cake samples***

Radiochim. Acta, revised manuscript submitted (Jan. 2011).

### 3.1 Investigation of the $^{236}\text{U}/^{238}\text{U}$ isotope abundance ratio in uranium ores and yellow cake samples

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Uranium ore, yellow cake,  $n(^{236}\text{U})/n(^{238}\text{U})$ , AMS

#### Abstract

Uranium ores and yellow cake samples of known geographic origin were investigated for their  $n(^{236}\text{U})/n(^{238}\text{U})$  isotope abundance ratio. Samples from four different uranium mines in Australia, Brazil and Canada were selected. Uranium was separated by UTEVA<sup>®</sup> Resin and was measured by Accelerator Mass Spectrometry (AMS) at the Vienna Environmental Research Accelerator (VERA). The measurement of the isotope abundance ratio  $n(^{236}\text{U})/n(^{238}\text{U})$  will be used to investigate possible correlations between the original mineral (uranium ore) and the intermediate product (yellow cake). Such correlations are useful indicators for nuclear forensic or for non-proliferation purposes.

#### Introduction

Illicit trafficking of nuclear and other radioactive material is a subject of serious concern due to the radiological hazard and the proliferation risks associated with such material. Nuclear forensics is a scientific discipline interfacing law enforcement, nuclear science and non-proliferation. Through nuclear forensic analysis, information on the history and on the potential origin of intercepted nuclear material can be obtained. The methods being used essentially focus on the measurements of the isotopic composition of the nuclear materials, the chemical composition, physical sample properties as well as their structure and

microstructure. The nuclear forensic signatures established so far are the best suited for identifying final products (e.g. pellets) while attributing intermediate products (e.g. yellow cakes) poses more challenges due to the lack of reference data [1]. Additionally, studies were performed to evaluate the applicability of chemical impurities of nuclear material as a characteristic signature for providing hints on the origin of the material [2]. This work focused on the determination of the isotopic ratio  $n(^{236}\text{U})/n(^{238}\text{U})$  in uranium ores and uranium ore concentrates ("yellow cakes") from Australia, Brazil and Canada. Uranium ores differ significantly in their chemical composition. This allows the pattern of chemical impurities to be used as characteristic signature. During ore processing, however, the accompanying elements are removed to a large extent and thus the respective signature tends to be wiped out. Uranium mining involves the removal from the ground of large quantities of ore containing uranium and its decay products. Depending on the geological specifics and on local environment conditions, mining can be carried out through either open pit, underground (main techniques) or in situ leaching. Open pit mining is used on ore bodies lying near to the surface. Underground mining becomes necessary for deposit depths of 50 – 200 m and more. In situ leaching does not require the removal of solid ore from the ground (compared to open pit and underground). For removing the uranium from the ore different leaching solutions can be used depending on the matrix composition of the rock [3,4]. Also for the subsequent chemical concentration and purification of the uranium different flow charts (involving different chemical processes) are in place. The final product is colloquially called "yellow cake". Most frequently this term describes ammonium diuranate  $[(\text{NH}_4)_2\text{U}_2\text{O}_7]$ , it may also be ammonium uranyl carbonate, uranium peroxide or uranium oxide. It contains 65 – 70% uranium and the radioactive uranium daughters have been removed to a large extent. Their concentrations in yellow cakes, however, depend on the chemical and physical processes used for uranium extraction and drying. Concentrations ranging from 0.06 to 5.3% depending on the radioisotope and chemical procedure (Momeni et al. [5] and references therein) have been observed. This intermediate product is further purified in order to obtain a final pure product of  $\text{U}_3\text{O}_8$  (> 99.98% pure) [6].

$^{236}\text{U}$  with a half-life of  $2.3 \times 10^7$  years [7] is produced via thermal neutron capture on  $^{235}\text{U}$ . In an ore, the neutrons are produced by spontaneous fission of  $^{238}\text{U}$  and by  $(\alpha, n)$  reactions on light elements (e.g. F, Na, Mg and Al) [8]. Due to its low isotope abundance in nature [9],  $^{236}\text{U}$  can only be measured by sophisticated mass spectrometry techniques. Isotopic ratios of  $n(^{236}\text{U})/n(^{238}\text{U})$  have been measured previously in several uranium ores [8,10-16]; the

obtained ratios vary between  $10^{-11}$  and  $10^{-9}$  (the latter, relatively high, value was found in ore samples from one of the natural fission reactors in Gabon [10]).

The present investigation focused on the uranium fraction in order to evaluate the possibility of using the minor abundant uranium isotopes as a nuclear forensic indicator. Reportedly, the  $n(^{235}\text{U})/n(^{238}\text{U})$  ratio shows only extremely small variations in nature and is thus not well suited as indicator. The  $n(^{234}\text{U})/n(^{238}\text{U})$  shows a larger variability, yet a number of coinciding values between different mines were observed [10]. The  $n(^{236}\text{U})/n(^{238}\text{U})$  ratio may be a similar marker of an uranium ore as the  $n(^{236}\text{U})/n(^{238}\text{U})$  depends very much on the actual characteristics of the ore body (U concentration, light element concentration, water content, etc.) an even larger variability between mines is to be expected. But on the other hand, it cannot be excluded that the same or similar ratios are achieved from different ore deposits. Up to now uranium ores were measured by several research groups [8,10-16]. Coinciding values of  $n(^{236}\text{U})/n(^{238}\text{U})$  ratios were measured for ores originating from Cigar Lake and from Joachimsthal, while pitchblende from Czech Republic were similar but pitchblende from Italy showed different results (up to one order of magnitude). Furthermore it is known from the literature that the production and thus the occurrence of e.g.  $^{36}\text{Cl}$  and  $^{239}\text{Pu}$  (both produced like  $^{236}\text{U}$  via neutron capture) is locally different and depends on the composition of the ore. It has been demonstrated in [17,18] that due to the ore characteristics the production parameters of the rare isotopes can change within a single borehole.

Therefore yellow cakes appear much more representative of a total ore body than a single rock sample because typically, several tons of samples are used to produce a batch of yellow cake. Consequently, differences between these uranium ore concentrates are more important as they are less prone to inhomogeneity.

As mentioned above, the  $n(^{236}\text{U})/n(^{238}\text{U})$  ratio is fairly small and so a sophisticated mass spectrometric measurement technique like accelerator mass spectrometry (AMS) is necessary. The detection limit for  $n(^{236}\text{U})/n(^{238}\text{U})$  with conventional mass spectrometry is  $\sim 10^{-10}$  (e.g. TIMS) [11]. AMS is the method of choice because of its very high abundance sensitivity and its ability to suppress background signals arising from molecular interferences. Only few specialized AMS facilities [8,13] are set up for measuring natural uranium. This study was carried out at the VERA facility and addresses the main question whether the ore and the intermediate product, the yellow cake, show the same isotopic ratio. To this end, four pairs of samples (uranium ore and yellow cake, i.e. feed and product of the same milling facility) were studied by AMS. The uranium concentration of the yellow cake samples is  $\sim 76\%$  and also the

grade of the ores does not show large variations (i.e. 0.1 - 0.5% in general). According to Richter et al. [10] uranium ore samples comparable to ours from Rabbit Lake, Ranger and Olympic Dam were measured by Thermal Ionisation Mass Spectrometry (TIMS) and the obtained  $n(^{236}\text{U})/n(^{238}\text{U})$  isotopic ratios were in the range of  $10^{-10} - 10^{-8}$ .

### Material and methods

For the chemical sample preparation all chemical reagents were prepared using deionized Milli-Q (18 M $\Omega$ •cm) water (Millipore, USA). 65% Suprapure HNO<sub>3</sub> was further purified by sub-boiling. To prevent cross-contamination (with natural uranium) during the chemical treatment, all laboratory equipment was leached with 10% sub-boiled HNO<sub>3</sub> at least for one day and washed three times with Milli-Q water, subsequently dried in a laminar flow bench and stored in clean zip bags. 30% HCl, 30% H<sub>2</sub>O<sub>2</sub> and 25% NH<sub>3</sub> were of Suprapure grade. The procedure for the separation of uranium in ores and yellow cakes using UTEVA<sup>®</sup> Resin is available from Eichrom Technologies, Inc. [19] and was modified to our needs. After leaching the uranium ore for three hours in 8M HNO<sub>3</sub>, the solution was filtered through a blue ribbon filter paper. The sample was evaporated to dryness, fumed three times with HNO<sub>3</sub>/H<sub>2</sub>O<sub>2</sub> and the residue was taken up in 3M HNO<sub>3</sub>. The yellow cake samples could be dissolved in 8M HNO<sub>3</sub> with gentle heating. Then the solution was taken to dryness and dissolved in 3M HNO<sub>3</sub>. The chromatographic column was loaded with 1.6 ml UTEVA<sup>®</sup> Resin (Eichrom Technologies, Inc.) and pre-conditioned with 3M HNO<sub>3</sub>. The sample solution was transferred to the column, washed with 3M HNO<sub>3</sub> and 5M HCl to remove Th and finally U was eluted with 1M HCl in a 50 ml vial. This solution was evaporated gently to dryness, taken up in 2 ml conc. HCl and the wall was washed with 7 ml deionised water. Finally, 1 ml Fe<sup>3+</sup> solution containing 1 mg Fe/ml was added. By slowly adding 25% NH<sub>3</sub> uranium was co-precipitated with Fe(OH)<sub>3</sub>. The solution was heated gently on a hot plate for about 15 minutes; the pH was reduced to 9. After centrifuging, the precipitate was dried at 100°C in an electric furnace for about 2 h. The dried precipitate was calcined at 800°C in small Quartz tubes. The resulting oxides samples were pressed into aluminium sample holders suitable for the ion source of VERA. Blank samples were prepared in parallel to the actual ore and yellow cake samples in order to verify the absence of tracers of uranium in the reagents or in the laboratory ware.

The VERA setup as used for actinide measurements is described in Vockenhuber et al. [20] and Steier et al. [21]. The uranium is sputtered with a Cs<sup>+</sup> beam, and in a first analysis  $^{236}\text{UO}^-$

(mass  $\sim 252$  amu) is selected; this ion is accompanied by molecular isobars, most abundant  $^{235}\text{U}^{16}\text{OH}^-$ . While conventional mass spectrometry (ICP-MS) cannot suppress this background sufficiently, AMS destroys the molecules by acceleration to high energies (3 MeV at VERA) and stripping to a high positive charge state in a dilute gas cell. After another stage of acceleration,  $^{236}\text{U}^{5+}$  at 18 MeV is selected in a second mass analysis. The ions are detected in a time-of-flight spectrometer and a final ionization chamber. Other ions can reach the detectors only on irregular trajectories, e.g. due to charge exchange on residual gas or scattering on surface in the spectrometer. VERA is optimised to suppress the most common types of such background [20]. However some complex processes – despite having very low possibilities – can be significant at the very low abundance of natural  $^{236}\text{U}$  ( $10^{-10}$  and below). One such background,  $^{235}\text{U}^{5+}$  from  $^{235}\text{U}^{16}\text{OH}^-$ , is discussed in [21]. The occurrence of such background depends on the chemical composition of the sputter material. While generally AMS is much less sensitive than other methods to the composition of the sample matrix, preparation of pure material prevents unexpected background. The time-of-flight and the particle energy measured by the detectors allowed in the cases observed so far to distinguish the background ions from  $^{236}\text{U}^{5+}$ ; however, the occurrence of an unexpected chemical element at high concentration in the matrix might raise new background processes, requiring dedicated systematic investigations.

To allow the determination of the ratio  $n(^{236}\text{U})/n(^{238}\text{U})$ , the first mass spectrometer is switched to measurements of  $^{238}\text{U}^{16}\text{O}^-$  once per second; this ion is measured as a beam current in a Faraday cup (typically 200 nA). Every five minutes  $^{238}\text{U}^{16}\text{O}^-$  is injected into the accelerator, and the  $^{238}\text{U}^{5+}$  current is measured in a Faraday cup in the second, high-energy mass spectrometer. By these means, the stripping yield of  $\text{U}^{5+}$  can be determined (typically 5%). The efficiency of the time-of-flight/ionisation detector (typically 25%) is determined using our in-house standard Vienna KkU ( $^{236}\text{U}/^{238}\text{U} = (6.98 \pm 0.32) \times 10^{-11}$ ) [16].

## Results and discussion

Ore samples from four different uranium mines (Olympic Dam, Ranger, Lagoa Real and Rabbit Lake) were analysed for their  $n(^{236}\text{U})/n(^{238}\text{U})$  isotopic ratio (Table 1). Additionally, two further samples from the Ranger mine were investigated. The grade of the latter was approximately 0.35% and the three samples from Ranger mine were sampled independently over a period of several weeks. The ore from Olympic Dam is geologically described as polymetallic hematite breccia complex deposit. The ore is exploited by open pit mining.

Ranger is an unconformity-Proterozoic fracture-bound deposit. The deposit consists of several ore bodies which were exploited subsequently. Lagoa Real is a metasomite; the ore is monometallic and the principal uranium mineral is uraninite. The deposit is exploited by open pit and underground mining. Rabbit Lake is also an unconformity-Proterozoic fracture-bound deposit. Several deposits in the area are exploited, mostly by open pit mining (with Eagle Point operating in underground mining). The mill (where the yellow cake is produced) accepts also ore from Cigar Lake.

Table 1: Results of  $n(^{236}\text{U})/n(^{238}\text{U})$  isotope abundance measurements in uranium ores. The measurement uncertainties are given in  $\pm 2s$ .

| Sample No. | Mine          | Country   | $n(^{236}\text{U})/n(^{238}\text{U})$ |
|------------|---------------|-----------|---------------------------------------|
| 73971      | Olympic Dam_4 | Australia | $(1.51 \pm 0.44) \times 10^{-11}$     |
| 73951      | Ranger_4      | Australia | $(1.92 \pm 0.28) \times 10^{-11}$     |
| 73950      | Ranger_3      | Australia | $(1.73 \pm 0.30) \times 10^{-11}$     |
| 73947      | Ranger_2      | Australia | $(1.76 \pm 0.30) \times 10^{-11}$     |
| BR11       | Lagoa Real    | Brazil    | $(4.12 \pm 0.04) \times 10^{-9}$      |
| 1425       | Rabbit Lake   | Canada    | $(1.12 \pm 0.06) \times 10^{-10}$     |

The obtained values were all in the range of  $10^{-11} - 10^{-9}$  which can be still attributed to natural uranium. According to Richter et al. [10] an uranium ore sample from Rabbit Lake was measured by Thermal Ionisation Mass Spectrometry (TIMS) with a detection limit of  $1.2 \times 10^{-10}$ . The obtained  $n(^{236}\text{U})/n(^{238}\text{U})$  isotopic ratio for Rabbit Lake was  $(2.8 \pm 1.7) \times 10^{-10}$ . Uranium ore samples from Ranger and Olympic Dam were investigated by Ovaskainen et al. [22] also via TIMS with an abundance sensitivity of few parts in  $10^{-8}$  and the obtained values of the ratio were less than  $1.45 \times 10^{-8}$ . At the VERA facility, systematic investigations suggest a detection limit for  $n(^{236}\text{U})/n(^{238}\text{U})$  below  $5 \times 10^{-12}$  for samples of 0.5 mg U [16]. Therefore more accurate results are to be expected. The samples from Australia have shown the lowest isotopic ratio while in Brazil (Lagoa Real) the ratio was two orders of magnitude higher. The obtained value with  $(4.12 \pm 0.04) \times 10^{-9}$  is surprisingly high. Up to now only from the natural reactor near Oklo (Gabon) a ratio in this range ( $9.32 \times 10^{-9}$ ) is known [10]. But we observe for this uranium ore from Lagoa Real a very high  $^{236}\text{U}$  count rate (compared to all other samples) which would suggest an anthropogenic contamination during the sample collection, sample storage, etc. However, an anthropogenic contamination during the chemical separation and sample preparation in our laboratories can be excluded because no significant blank contribution or cross-contamination could be noticed in the blank samples. The results from Ranger\_2 to Ranger\_4 show no significant differences (consistent within 2s).

The  $n(^{236}\text{U})/n(^{238}\text{U})$  ratio measured in the Rabbit Lake ore sample is significantly lower than the values measured from the two Australian ores (Olympic Dam and Ranger mine). Yet, the value is in the same order of magnitude as previously measured by Zhao et al. [15] and Berkovits et al. [11] and their values were  $(5.6 \pm 1.5) \times 10^{-10}$  and  $(3.3 \pm 0.5) \times 10^{-10}$ , respectively. In Table 2 the  $n(^{236}\text{U})/n(^{238}\text{U})$  ratios of the yellow cake samples are shown. All of them are at the level of few parts in  $10^{-11}$ . The results of the chemically treated yellow cake sample fit with the order of magnitude of the isotopic ratio of the uranium ore (Table 1) with the exception of Lagoa Real. Here the yellow cake seems to be more reliable and confirm our suggestion of a contamination of the ore sample investigated above. The isotopic ratio of the uranium ore from Rabbit Lake is a factor of 2 higher than the ratios obtained from the yellow cakes (Table 2 and 3). This can be explained by the fact that the mine exploits several deposits and the mill accepts also ore from other mines. This leads to an isotopic inhomogeneity of the material being processed. In consequence, the single sample of uranium ore which was investigated does not necessarily correspond to the yellow cake sample provided by the same facility. The same might be true for the uranium ore from Olympic Dam which shows a slightly smaller value than the yellow cake samples. For the samples from Ranger mine an excellent agreement of the  $n(^{236}\text{U})/n(^{238}\text{U})$  ratios between the ore and yellow cake material can be noticed.

Table 2: Results of  $n(^{236}\text{U})/n(^{238}\text{U})$  isotope abundance ratio measurement in yellow cake samples (with chemical sample preparation prior to AMS measurement). The measurement uncertainties are given in  $\pm 2s$ .

| Sample No. | Mine        | Country   | $n(^{236}\text{U})/n(^{238}\text{U})$ |
|------------|-------------|-----------|---------------------------------------|
| 28         | Olympic Dam | Australia | $(4.46 \pm 0.48) \times 10^{-11}$     |
| 24         | Ranger      | Australia | $(1.48 \pm 0.26) \times 10^{-11}$     |
| 15         | Lagoa Real  | Brazil    | $(3.09 \pm 0.38) \times 10^{-11}$     |
| 51         | Rabbit Lake | Canada    | $(5.17 \pm 0.48) \times 10^{-11}$     |

Complementary to the measurements described above (with chemical separation of the uranium prior to AMS measurement), the four yellow cakes were subjected to two additional measurements (independent sample preparation, two separated beam times, Table 3) directly by AMS without any chemical separation of the uranium; the samples were only calcined at 800°C and pressed into aluminium sample holders.

Table 3: Results of  $n(^{236}\text{U})/n(^{238}\text{U})$  isotope abundance ratio measurement in yellow cake samples (without chemical sample preparation prior the AMS measurement). The measurement uncertainties are given in  $\pm 2\text{s}$ . March 2010 and May 2010 denote two independent measurements at different times.

| Sample No. | Mine        | Country   | $n(^{236}\text{U})/n(^{238}\text{U})$ | $n(^{236}\text{U})/n(^{238}\text{U})$ |
|------------|-------------|-----------|---------------------------------------|---------------------------------------|
|            |             |           | March 2010                            | May 2010                              |
| 28         | Olympic Dam | Australia | $(3.76 \pm 0.52) \times 10^{-11}$     | $(3.90 \pm 0.70) \times 10^{-11}$     |
| 24         | Ranger      | Australia | $(1.14 \pm 0.40) \times 10^{-10}$     | $(1.30 \pm 0.78) \times 10^{-10}$     |
| 15         | Lagoa Real  | Brazil    | $(2.66 \pm 1.30) \times 10^{-11}$     | $(1.54 \pm 0.46) \times 10^{-11}$     |
| 51         | Rabbit Lake | Canada    | $(5.40 \pm 0.56) \times 10^{-11}$     | $(4.70 \pm 0.48) \times 10^{-11}$     |

The  $n(^{236}\text{U})/n(^{238}\text{U})$  ratios as measured in the (unseparated) replicate samples from Olympic Dam and Ranger agree very well and also the isotopic ratios of the two independent measurements on the Rabbit Lake sample agree within the stated uncertainty. The results obtained for Lagoa Real suggest small differences though statistically not significant (Table 3). By comparing the separated uranium fractions with the untreated samples one can notice that all samples, except Ranger, are in good agreement. The isotopic ratios of the separated uranium fraction of Olympic Dam and Rabbit Lake agree very well with the directly measured samples. The value for  $n(^{236}\text{U})/n(^{238}\text{U})$  from the chemically treated Ranger samples is an order of magnitude lower than the directly measured samples. This could be explained by an isobaric interference arising from  $^{232}\text{Th}$ ; a significant current of  $^{232}\text{Th}^{16}\text{O}^-$  (about one percent of the  $^{238}\text{U}^{16}\text{O}^-$  current) was indeed observed in the first mass spectrometer of VERA for the Ranger samples without chemical treatment. Further investigations would be required to rule out that  $^{232}\text{Th}$  can interfere with the  $^{236}\text{U}$  measurement.

## Conclusion

The  $^{236}\text{U}$  production in uranium ores depends on the neutron flux as well as on the probability of neutron capture by uranium isotopes. The main sources of neutrons are the spontaneous fission of  $^{238}\text{U}$  and  $(\alpha, n)$ -reactions on light elements (e.g. Li, Be, Na, etc). The presence of water and neutron absorbers like Gd and Sm influence the build up of  $^{236}\text{U}$  [14]. In consequence, a mine-to-mine variability of the  $n(^{236}\text{U})/n(^{238}\text{U})$  ratio should be expected and it might serve as candidate parameter for tracing the origin of natural uranium. The set of uranium ore samples we studied by means of AMS measurements indeed showed a mine-to-mine variability of the  $n(^{236}\text{U})/n(^{238}\text{U})$  ratio. Uranium ores are, however, not homogeneous and analysing one ore sample per mine results only in a local isotopic composition. For one mine (Ranger), three different samples were investigated and they agree within 2s. Four pairs

of samples (uranium ore and yellow cake, i.e. feed and product of the same milling facility) were studied by AMS for their  $n(^{236}\text{U})/n(^{238}\text{U})$  isotope abundance ratio and the possible usage of  $^{236}\text{U}$  as an indicator for establishing a relation between the ore and the yellow cake. In this study, yellow cake samples with and without chemical treatment prior to AMS measurements were investigated. The isotopic ratio  $n(^{236}\text{U})/n(^{238}\text{U})$  of the yellow cake samples after the chemical separation reflects a typical profile (average value) of the yellow cake sample and isobaric interferences are not to be expected. The  $n(^{236}\text{U})/n(^{238}\text{U})$  ratio obtained on the samples without chemical treatment (prior to measurement) confirm those observations, with the exception of the Ranger material. The latter is apparently suffering from an isobaric interference, which increases the  $n(^{236}\text{U})/n(^{238}\text{U})$  ratio by one order of magnitude. Comparing the  $n(^{236}\text{U})/n(^{238}\text{U})$  ratios measured in the ore samples to those obtained for the respective yellow cake samples, we observe a good correlation only for the materials from Ranger mine. The three other sample pairs do not correlate. This observation, though obtained for a small sample population only, suggest that for tracing the origin of natural uranium, yellow cake samples should be taken as starting point rather than uranium ores. This eliminates to some extent the variability arising from inhomogeneity in the ore body, which reflects in the  $n(^{236}\text{U})/n(^{238}\text{U})$ . Moreover, the fact the uranium mills may process material from various deposits and often accept ore from different mines leads to blending of material and in consequence to an average value of the isotope ratio.

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### 3.1.1 Supplementary investigations

#### *Introduction*

O. Hahn, L. Meitner and F. Strassmann discovered the nuclear fission. That the tremendous release of energy could be achieved both for energy production and nuclear explosives was soon clear. For both applications further developments were necessary and therefore appropriate research programs were launched; in the United States under the scientific guidance of R. Oppenheimer and in Germany of W. Heisenberg and K. Diebner (two independent groups) [76].

Three pre-nuclear uranium samples, namely a Wirtz plate, a Heisenberg cube and a yellow cake sample from Otto Hahn, were investigated for the  $^{236}\text{U}/^{238}\text{U}$  isotopic ratio by AMS. For these samples no further chemical treatment was carried out, except an acid leaching to remove any anthropogenic contamination during storage. Only the yellow cake sample was divided into two sub-samples; one was chemically treated for the uranium separation by UTEVA<sup>®</sup> resin.

The history and nuclear forensic investigations of the Heisenberg cube and Wirtz plate are well documented in [76]. The uranium isotope measurements had been conducted by Thermal Ionization Mass Spectrometry (TIMS). In none of these samples a  $^{236}\text{U}$  ion current above the detection limit could be recorded. The  $^{236}\text{U}/^{238}\text{U}$  isotopic ratio for the Heisenberg cube and the Wirtz plate was  $< 2.0 \times 10^{-10}$  and  $< 1.3 \times 10^{-10}$ , respectively.

Furthermore these investigations have shown that both samples were manufactured using ore from Joachimstal. An important parameter for nuclear forensic is the date of the last chemical purification of uranium. It provides information on the authenticity of these samples and on their production dates. For the age determination the  $^{234}\text{U}/^{230}\text{Th}$  ratio was used. For the Heisenberg cube a production date of September 1943  $\pm$  0.5 years and for the Wirtz plate August 1940  $\pm$  0.2 years were found [76].

The yellow cake sample of O. Hahn was found at the Johannes Gutenberg University Mainz. It is conceivable that this sample originally came from F. Strassmann.

TIMS can achieve bulk sensitivities down to about  $^{236}\text{U}/\text{U} \sim 10^{-10}$  [25] and these samples have shown an isotopic ratio in this range. Therefore it was suggested to measure them by AMS at VERA because systematic investigations suggest a detection limit for  $^{236}\text{U}/^{238}\text{U}$  below  $5 \times 10^{-12}$  for samples of 0.5 mg U [20].

*Materials and methods*

The advantage of these samples is that they were produced long before any sources of anthropogenic nuclides in the environment occurred, like the global fallout from atmospheric weapons testing during the 1950s and 1960s or the reactor accident at Chernobyl on April 26<sup>th</sup> (1986).

All chemical reagents were prepared using deionized Milli-Q (18 M $\Omega$ ·cm) water (Millipore, USA). 65% Suprapure HNO<sub>3</sub> was purified by distillation. To prevent cross-contamination (from natural uranium) during the chemical treatment, all the material was stored in 10% HNO<sub>3</sub> at least for one day and washed three times with Milli-Q water, dried in a laminar flow bench and stored in clean zip bags. 30% HCl and 30% H<sub>2</sub>O<sub>2</sub> were of Suprapure grade.

The yellow cake sample of Otto Hahn was divided in two sub-samples: one for the direct measurement by AMS (named O. Hahn) and one part was taken for the chemical separation of uranium using UTEVA<sup>®</sup> resin (labelled O. Hahn\_1). The method is available from Eichrom Technologies, Inc. [48] which was modified to our needs; it is described in detail in chapter 5 “Appendix A” and Srnecik et al. [27], respectively.

The samples were weighed in 2 ml tubes (values see Table 7) in a glove box for naturally uranium and thorium. To remove any potential anthropogenic contamination from the surface the Heisenberg cube and Wirtz plate sample were cleaned to following procedure: the metals were put separately in 2 ml container filled with 3M HNO<sub>3</sub>. The samples were removed from the acid solution when a slightly yellow solution occurred. Afterwards the samples were washed twice with Millipore water and then they were transferred to an empty 2 ml container (already weighted and with the appropriate name on it) and dried by air over night.

**Table 7.** Material data

| Sample code     | Weight dry [mg] | Notes                   |
|-----------------|-----------------|-------------------------|
| Heisenberg cube | 50.1            |                         |
| Wirtz plate     | 31.8            |                         |
| O. Hahn         | 62.3            | for AMS                 |
| O. Hahn_1       | 51.0            | for chemical separation |

A sub-sample was taken from Heisenberg cube, Wirtz plate and O. Hahn samples and was combusted at 800°C for 2 h in a muffle furnace.

### Results and discussion

The samples Heisenberg cube and Wirtz plate had been already measured at the ITU and the obtained results were  $< 2.0 \times 10^{-10}$  and  $< 1.3 \times 10^{-10}$  [76], respectively. The samples without chemical treatment prior to AMS measurement were prepared for two separate beam times. In Table 8 the AMS results are presented. All samples which were measured twice are consistent within  $1\sigma$ . The two sub-samples from O. Hahn (with and without chemical separation of the uranium prior to AMS measurement) agree very well within  $1\sigma$ .

**Table 8.** AMS results of pre-nuclear samples. The measurement uncertainty is given in  $\pm 1\sigma$ .

| Sample          | March                             | May                               |
|-----------------|-----------------------------------|-----------------------------------|
|                 | $^{236}\text{U}/^{238}\text{U}$   | $^{236}\text{U}/^{238}\text{U}$   |
| Heisenberg cube | $(1.06 \pm 0.05) \times 10^{-10}$ | $(1.00 \pm 0.04) \times 10^{-10}$ |
| Wirtz plate     | $(1.12 \pm 0.05) \times 10^{-10}$ | $(1.03 \pm 0.07) \times 10^{-10}$ |
| O. Hahn         | $(1.14 \pm 0.05) \times 10^{-10}$ | $(9.57 \pm 0.96) \times 10^{-11}$ |
| O. Hahn_1       |                                   | $(9.66 \pm 0.29) \times 10^{-11}$ |

The obtained results of the Heisenberg cube and Wirtz plate show that both materials had not been irradiated and due to the corresponding  $^{236}\text{U}/^{238}\text{U}$  ratio the materials probably were produced from the same uranium ore.



***Determination of the isotopic ratio  $^{236}\text{U}/^{238}\text{U}$   
in Austrian water samples***

Nucl. Instrum. Meth. B **268** (2010) 1146 – 1149.

### 3.2 Determination of the isotopic ratio $^{236}\text{U}/^{238}\text{U}$ in Austrian water samples

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#### Abstract

$^{236}\text{U}$  with a half life of  $2.3 \cdot 10^7$  years is naturally produced in ultra-trace amounts ( $^{236}\text{U}/^{238}\text{U} < 10^{-10}$ ) in ores, soils and rocks, while a huge amount has been produced in nuclear power plants and possibly nuclear weapons tests by man. Thus, anthropogenic uranium may cause a significant measurement background for geological applications of natural  $^{236}\text{U}$ . To investigate this background, water samples from rivers, creeks and wells were collected in the alpine region of Forstau (Salzburg, Austria) and from surrounding areas. Thin sources for alpha spectrometry were prepared by anion exchange and co-precipitation with  $\text{NdF}_3$  to determine the  $^{238}\text{U}$  concentration. These filters were reprocessed for the analysis of the isotopic ratio  $^{236}\text{U}/^{238}\text{U}$  by AMS. The special aim was the characterization of the  $^{236}\text{U}/^{238}\text{U}$  ratio in natural waters and the investigation of contributions from anthropogenic sources. Our measurements of  $^{236}\text{U}$  in Austrian water samples from wells, rivers and creeks show the first data on the spreading of anthropogenic  $^{236}\text{U}$  in the general environment far from local contamination sources.

PACS: 93.85.Np; 91.65.Dt; 07.75.+h

Keywords:  $^{236}\text{U}/^{238}\text{U}$ , natural waters, AMS

## Introduction

$^{236}\text{U}$  with a half life of  $2.3 \cdot 10^7$  years is continuously produced via thermal neutron capture on the isotope  $^{235}\text{U}$  which is present in uranium ores, soils and rocks. Natural production results from neutrons produced by ( $\alpha$ ,n)-reactions on lighter nuclides, spontaneous fission of  $^{238}\text{U}$ , induced fission of  $^{235}\text{U}$  and at the earth's surface from cosmic rays [1,2]. The natural ratio in river water is expected to be between  $1 \cdot 10^{-14}$  and  $1 \cdot 10^{-13}$  [3]. Additionally, a huge amount ( $\sim 10^6$  kg, [3]) has been produced by man in nuclear power plants. However, the extend to which this has been dispersed into the general environment is as yet unclear. Our main aim was to probe for the first time whether anthropogenic  $^{236}\text{U}$ , which up to now has only been detected near known contaminated sites [4,5,6], is present also in the "typical" environment.

The northern foothills of the Alps in Austria was one of the regions in western Europe which was most heavily affected by fallout from the Chernobyl accident, with  $^{137}\text{Cs}$  depositions of  $50 \text{ kBq/m}^2$  or even higher [7]. The deposition shows a strong regional variation of up to 1:100, controlled by the rainfall pattern. The mean inventory of  $^{137}\text{Cs}$  from global fallout was  $2.3 \text{ kBq/m}^2$  at the time of the Chernobyl accident. Well and rivulet water from this area were chosen for our first investigations and were expected to provide data on the average  $^{236}\text{U}$  contamination throughout their feeding area because uranium generally shows good water solubility. Measurements on river sediments from the Garigliano river (Southern Italy) had not shown  $^{236}\text{U}$  levels above the laboratory background in a previous investigation [8]. Compared to ore samples [2] with a large uranium content, the measurement of these low-concentration natural samples depends strongly on sensitivity and background, and the samples require a more complex preparation procedure.

Mineral waters which stem from very deep aquifers generally show a high amount of natural radionuclides compared to surface water and water from shallower wells; to date artificial nuclides have not been found in these very old, deeply stored waters [9]. An example of this water type is well water from inside the Badgastein radon healing gallery (Salzburg, Austria), which was also investigated here.

## Materials and methods

Water samples were collected in different regions of Austria as shown in figure 1. These were mainly in Salzburg and Styria but also in Lower and Upper Austria from rivers, creeks and wells. A uranium mine existed more than 20 years ago near the sampling site in Forstau (Salzburg), and studies have shown that in this area relatively higher uranium concentrations

can be found in river and spring waters [10]. We collected samples in this region from a well (Fahlhaus) and from a river (Forstaubach).

### *Sample preparation and measurements*

Water samples of 1.5 L and up to 5 L were collected and acidified with an appropriate amount of 7.2 M HNO<sub>3</sub>, and a <sup>232</sup>U spike (NIST SRM 4324B, 1.443 ± 0.009 Bq/mL, reference date September 30, 2006) was added. Two different resins (Dowex 1x2, Dow Chemical Co. and UTEVA, Eichrom Technologies, LLC) were used for uranium separation.

### *Separation by Dowex 1x2*

After adding 20 µL of the <sup>232</sup>U tracer the water samples were evaporated to dryness and fumed three times with conc. HNO<sub>3</sub> and three times with conc. HCl. In some cases after the HNO<sub>3</sub> fuming step it was also necessary to fume the samples with conc. HF because of the presence of large amounts of silica acid. Where the HF step was necessary the samples were fumed several times with H<sub>3</sub>BO<sub>3</sub> (c = 5g/100 mL), then with HNO<sub>3</sub>/H<sub>2</sub>O<sub>2</sub> and finally with conc. HCl. The residue was dissolved in 80 mL 8 M HCl, loaded onto the column (Dowex 1x2, 100 – 200 mesh, Cl<sup>-</sup> form) and washed twice with 25 mL 8M HCl to remove Th and Ca. Uranium was eluted with 90 mL 0.1M HCl [11].

### *Separation by UTEVA*

The procedure for the determination of uranium in water using UTEVA available from Eichrom Technologies, LLC [12] was modified to our needs. After adding the <sup>232</sup>U spike the water sample was evaporated to maximally 200 mL, 0.5 mL of 1.25M Ca(NO<sub>3</sub>)<sub>2</sub> was added and the sample heated until boiling. Phenolphthalein indicator and 200 µL of 3.2M (NH<sub>4</sub>)<sub>2</sub>HPO<sub>4</sub> were added followed by conc. NH<sub>4</sub>OH to reach the phenolphthalein end point and formation of Ca<sub>3</sub>(PO<sub>4</sub>)<sub>2</sub> (pH 8 - 10). The sample was heated for 30 min and the precipitate was allowed to settle over night. If it was not possible to decant most of the supernatant, the solution was transferred stepwise to a 50 mL centrifuge tube and centrifuged 30 min at 4 000 rpm (the relative centrifugal force (RCF) is 1646). The precipitate was washed three times with Millipore water (approximately twice the volume of the precipitate) and was centrifuged for another 20 min at 4 000 rpm. It was then dissolved in 10 mL conc. HNO<sub>3</sub>, transferred to a 100 mL beaker, 4 mL H<sub>2</sub>O<sub>2</sub> was added and the solution evaporated to dryness. This step was repeated with another 10 mL conc. HNO<sub>3</sub>. The residue was dissolved in 15 mL 3M HNO<sub>3</sub> –

1M  $\text{Al}(\text{NO}_3)_3$  and any insoluble residua centrifuged off (20 min at 4 000 rpm). A column filled with 0.5 g of UTEVA (100 – 150  $\mu\text{m}$ ) was conditioned with 3M  $\text{HNO}_3$  before the sample was transferred to the column. The beaker was rinsed with 5 mL and then three times with 10 mL of 3M  $\text{HNO}_3$ . To convert the resin to the chloride form 10 mL of 9M  $\text{HCl}$  was loaded onto the column, and after adding (three times) 10 mL 5M  $\text{HCl}$  – 0.05M oxalic acid to remove Np, Pu and Th, uranium was eluted with 30 mL of 0.01M  $\text{HCl}$ .

#### *Microprecipitation*

The uranium fraction was evaporated to dryness, fumed three times with 5 mL conc.  $\text{HNO}_3$  and 2 mL  $\text{H}_2\text{O}_2$  and three times with 5 mL conc.  $\text{HCl}$ . The residue was taken up in 20 mL 1M  $\text{HCl}$  and 50  $\mu\text{L}$  of  $\text{Nd}^{3+}$  solution ( $c = 1 \text{ mg/mL}$ ), 100  $\mu\text{L}$  of 15 %  $\text{TiCl}_3$  solution (for uranium reduction) and 5 mL 40 %  $\text{HF}$  were added [13,14]. After one hour the solution was filtered through a cellulose nitrate membrane filter (Whatman<sup>®</sup>, 0.1  $\mu\text{m}$  pore size) and the  $\text{NdF}_3$  precipitate washed three times with 2 mL 4 %  $\text{HF}$  and twice with 2 mL Millipore water.

#### *Alpha measurement*

Alpha spectrometry was performed using a PIPS (Passivated Implanted Planar Silicon) Detector, Model 7401 VR, Canberra/Packard with an active area of 450  $\text{mm}^2$ . The counting time was 252 000 s and for these measurements, the detection limits, calculated according to Currie [15], were 0.3 mBq/sample for  $^{238}\text{U}$ . The software Genie 2.1 (Canberra, USA) was used to evaluate the spectra.

#### *AMS measurement*

For the AMS measurement the filters already analysed by alpha spectrometry were reprocessed according to Srncik et al. [16]. The procedure consists of re-dissolving the precipitate with  $\text{HNO}_3$ , co-precipitation with iron hydroxide, and combustion to oxides which are pressed into an aluminium sample holder either with or without silver as binder. The VERA setup as used for actinide measurements is described in Vockenhuber et al. [17]. Molecular  $\text{UO}^-$  ions are extracted from the solid sample in the caesium sputter source. The low-energy mass spectrometer selects  $^{236}\text{U}^{16}\text{O}^-$ . Gas stripping at 3 MV terminal voltage efficiently removes any molecular isobars (especially  $^{235}\text{UH}^-$ ). The stripping yield achieved is about 5 % for  $\text{U}^{5+}$ . The ions of interest and any interfering ions which pass all beam filters are identified with a high resolution time-of-flight system with 2.8 m flight path, a time resolution

of 0.7 ns (FWHM) for  $^{238}\text{U}$  at 18 MeV and a transmission of 30%. The energy is then measured in an ionization chamber.

### Results and discussion

Initially we measured four different volumes (0.1 L, 0.3 L, 1 L and 3L) of water from the radon gallery in Badgastein (Salzburg, Austria) because it is the well with the highest known content of  $^{238}\text{U}$  in Austria ( $\sim 88 \mu\text{g/L}$ ), and the clearly pre-anthropogenic  $^{236}\text{U}/^{238}\text{U}$  isotopic ratio is already known from previous measurements ( $\sim 6.6 \cdot 10^{-12}$  [3]). The obtained values are shown in table 1 to be between  $10^{-11}$  and  $10^{-9}$ ; they do not agree with the previously reported, clearly lower value. We attribute this to differences between the sample preparation procedures in the past and now: no spike was added to the earlier samples and they had not passed through a neodymium co-precipitation step. A much simpler separation with Dowex 1x8 had been performed, which the high uranium concentration in Badgastein water makes possible, but this is not applicable for the low-concentration and large volume samples which are the target of this project. The previously used laboratory is no longer available, and all laboratory ware and reagents have been changed. To assess whether the  $^{232}\text{U}$  spike contains  $^{236}\text{U}$ , a 20  $\mu\text{L}$  spike solution was co-precipitated with iron hydroxide and measured by AMS. The result obtained corresponds to  $(9 \pm 8) \cdot 10^7$  atoms of  $^{236}\text{U}$ , whereas a sputter target prepared from directly combusted pure iron gave no  $^{236}\text{U}$  counts. The value for the spike is unexpectedly high, but too low to explain the high isotopic ratios obtained for the new Badgastein samples, thus an additional background contribution during later steps of the sample preparation exists. Further investigations will be performed to reduce the background, but, as discussed in the results section below, the present level is sufficiently low for investigations of anthropogenically influenced surface water. The results of the isotopic ratio  $^{236}\text{U}/^{238}\text{U}$  measured by AMS are given in table 2 and figure 2. All ratios are higher than the natural ratio ( $< 10^{-10}$ ). If we subtract the laboratory background of about  $10^8$   $^{236}\text{U}$  atoms per sample (black line in figure 2), several of the samples show a  $^{236}\text{U}$  content significantly above our background line estimated from the Badgastein water (figure 2); especially remarkable is the value of Irxwasser with an atomic ratio of  $(4.57 \pm 0.03) \cdot 10^{-5}$ . Two especially small samples show a  $^{236}\text{U}/^{238}\text{U}$  value lower than the background; we attribute this to a bad reproducibility of the background. Generally, no correlation is visible between the  $^{236}\text{U}$  and the  $^{238}\text{U}$  concentration, which is in agreement with the assumption that the (anthropogenic)  $^{236}\text{U}$  and the (natural)  $^{238}\text{U}$  originate from different sources.

## Conclusion

Our measurements of  $^{236}\text{U}$  in water samples from wells and rivulets in Austria have yielded the first data on the dispersion of anthropogenic  $^{236}\text{U}$  in the general environment far from local contamination sources, and demonstrate that AMS can reach the required sensitivity levels, which are generally too low for other methods. The  $^{238}\text{U}$  concentrations range from 0.019  $\mu\text{g/L}$  (Liegnitz, Salzburg) up to 6.85  $\mu\text{g/L}$  (Kamegg4, Lower Austria), while the  $^{236}\text{U}$  levels range from  $4.14 \cdot 10^6$  atoms/L to  $2.14 \cdot 10^9$  atoms/L.

Several samples show  $^{236}\text{U}/^{238}\text{U}$  ratios considerably higher than the natural ratio. We think that we see in Austria an almost omnipresent  $^{236}\text{U}$  contamination from global fallout and/or from Chernobyl. The absence of a second anthropogenic isotope of uranium (as it exists e.g. in the case of Cs or Pu) makes the assessment of the source for a single sample difficult. Our small first data set does not yet allow us to determine whether the  $^{236}\text{U}$  contamination is correlated with the spatial pattern of  $^{137}\text{Cs}$  fallout from Chernobyl.

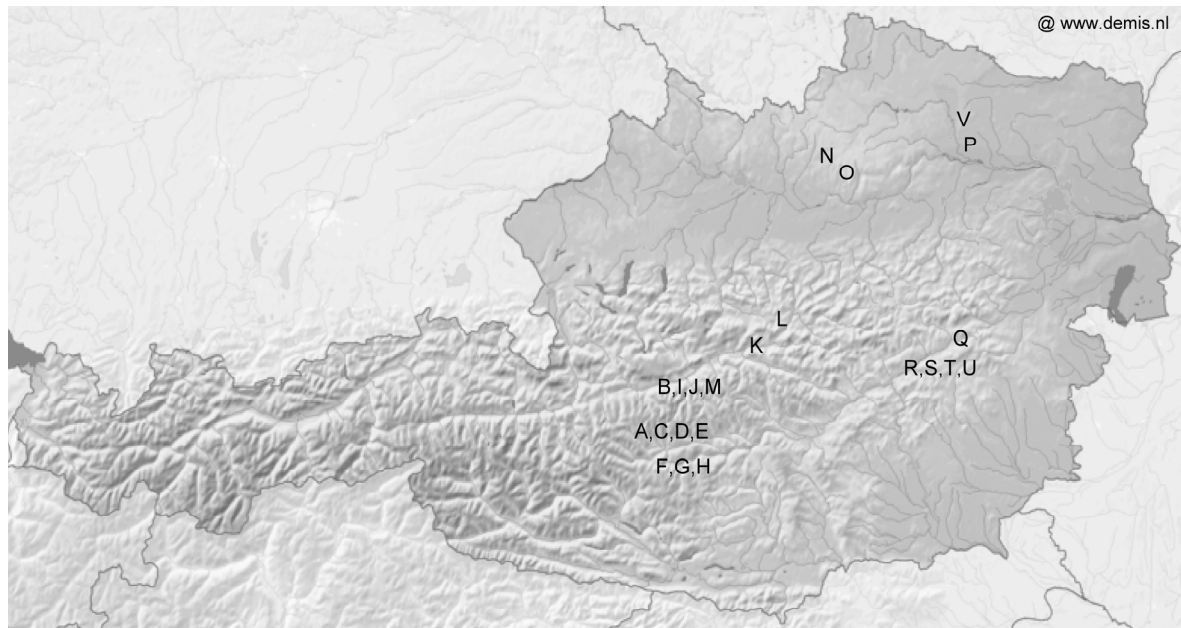
The unexpectedly high laboratory background of around  $10^8$  atoms  $^{236}\text{U}$  per sample is perhaps a further indication of the widespread distribution of anthropogenic uranium, which was undetectable before the development of suitable AMS methods. Screening of all used laboratory ware and reagents for  $^{236}\text{U}$  contamination will be necessary to reduce the background to the levels required for the much lower natural isotopic ratios. Further measurements will be performed to obtain a general overview of the environmental distribution of anthropogenic  $^{236}\text{U}$ , and to identify its main sources.

## Acknowledgement

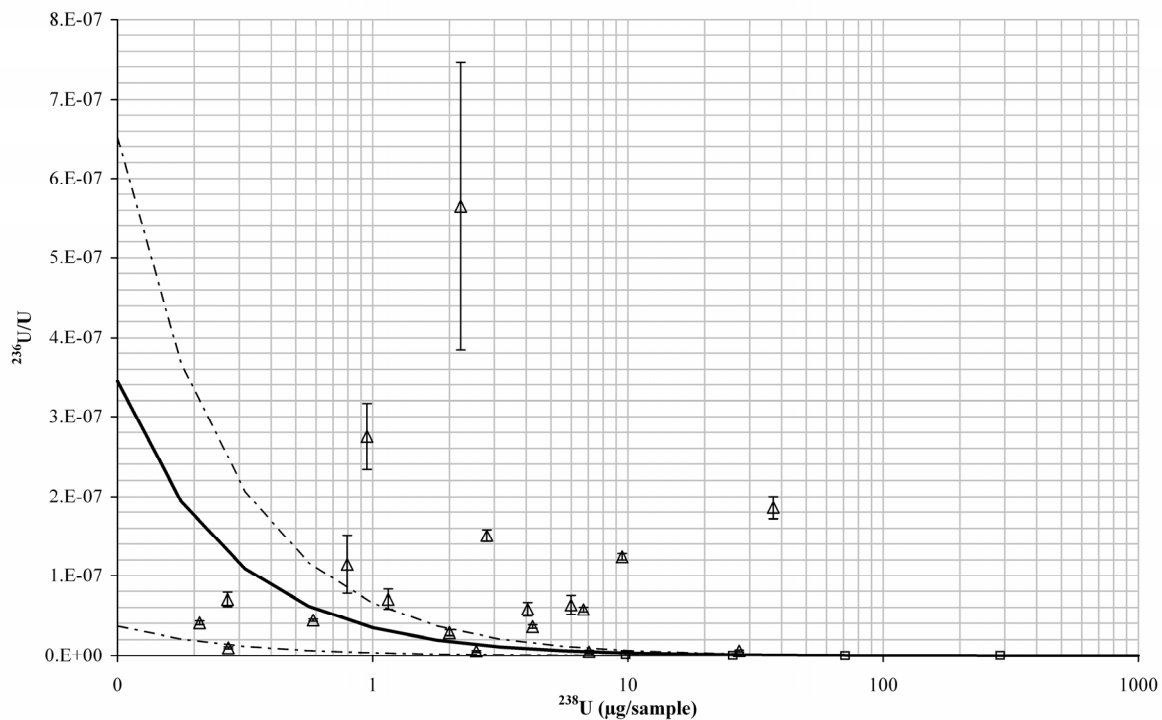
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**Figures****Figure 1.** Sampling sites (a description of the alphabetic character is given in table 2).

**Figure 2.** The isotopic ratio  $^{236}\text{U}/\text{U}$  determined by AMS versus the total amount of  $^{238}\text{U}$  determined by alpha spectrometry. The open squares show the Gasteiner water and the open triangles represent all other water samples. The black line indicates the background whereas the uncertainty is shown by a dashed line. The error bars of the mass (x – direction) are smaller than the point size. The uncertainty of the blank correction is not included in the error bars of the points. One sample [Irxwasser,  $(4.57 \pm 0.39) \cdot 10^{-5}$ ] is too high to be shown in the plot.



### Tables and diagrams

**Table 1.** Isotopic ratio of  $^{236}\text{U}/^{238}\text{U}$  from the Badgastein Water.

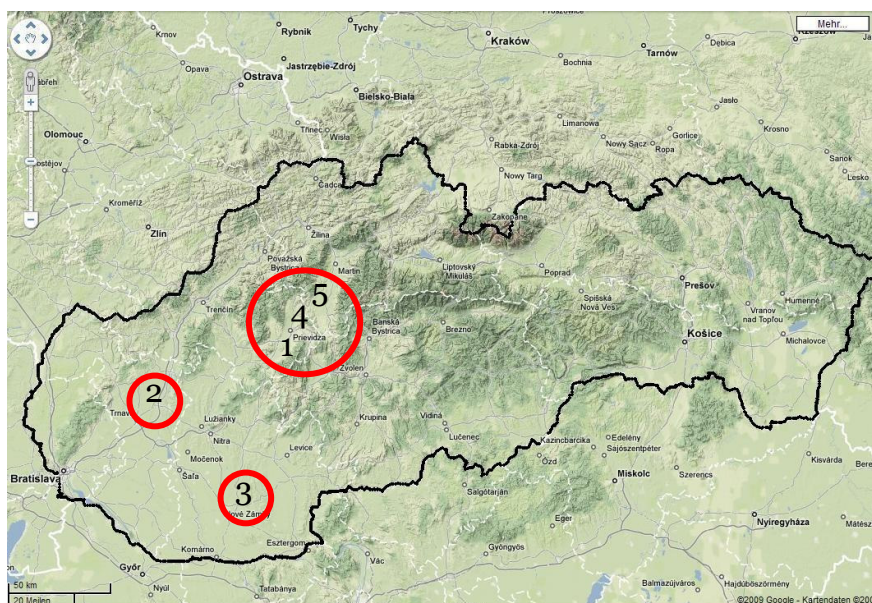
| Sample    | $^{236}\text{U}/^{238}\text{U}$  |
|-----------|----------------------------------|
| GastW0.1L | $(1.06 \pm 0.19) \cdot 10^{-9}$  |
| GastW0.3L | $(7.11 \pm 1.22) \cdot 10^{-10}$ |
| GastW1L   | $(3.03 \pm 0.40) \cdot 10^{-11}$ |
| GastW3L   | $(2.42 \pm 0.21) \cdot 10^{-11}$ |

**Table 2.** The isotopic ratio of  $^{236}\text{U}/^{238}\text{U}$  by AMS in Austrian water samples. The measurement uncertainties are given in  $\pm 1\sigma$ .

| Map position | Sample                       | $^{236}\text{U}/^{238}\text{U}$ | Volume (L) | chem. yield (%) | $^{238}\text{U}$ ( $\mu\text{g/L}$ ) |
|--------------|------------------------------|---------------------------------|------------|-----------------|--------------------------------------|
| A            | Brandgrabenbach              | $(6.29 \pm 1.19) \cdot 10^{-8}$ | 1.5        | $97 \pm 13$     | 0.18                                 |
| B            | Forstaubach                  | $(6.99 \pm 0.92) \cdot 10^{-8}$ | 1.5        | $81 \pm 7$      | 0.39                                 |
| C            | Gengitschhütte               | $(2.12 \pm 1.46) \cdot 10^{-8}$ | 1.5        | $56 \pm 5$      | -                                    |
| D            | Kerngrabenbach               | $(4.37 \pm 0.13) \cdot 10^{-8}$ | 1.5        | $86 \pm 8$      | 2.7                                  |
| E            | Liegnitz                     | -                               | 1.5        | $61 \pm 6$      | 0.019                                |
| F            | Purngrabenbach               | $(5.76 \pm 0.85) \cdot 10^{-8}$ | 1.5        | $60 \pm 8$      | 0.53                                 |
| G            | Taurach Süd                  | $(4.04 \pm 0.25) \cdot 10^{-8}$ | 1.5        | $43 \pm 4$      | 0.83                                 |
| H            | Reitbach                     | $(1.14 \pm 0.37) \cdot 10^{-8}$ | 1.5        | $82 \pm 11$     | 0.14                                 |
| I            | Fahlhaus                     | $(5.95 \pm 1.27) \cdot 10^{-9}$ | 4.424      | $86 \pm 11$     | 5.46                                 |
| J            | Preuneggbach                 | $(5.36 \pm 1.12) \cdot 10^{-9}$ | 4.887      | $73 \pm 6$      | 1.90                                 |
| K            | Enns/Weißbach                | $(1.51 \pm 0.07) \cdot 10^{-7}$ | 4.959      | $67 \pm 6$      | 0.56                                 |
| L            | Marienwaldweg                | $(2.84 \pm 0.36) \cdot 10^{-8}$ | 4.887      | $55 \pm 5$      | 0.51                                 |
| M            | Enns/Warterdorf              | $(4.65 \pm 2.28) \cdot 10^{-9}$ | 4.917      | $28 \pm 3$      | 1.41                                 |
| N            | Irxwasser                    | $(4.57 \pm 0.39) \cdot 10^{-5}$ | 4.392      | $58 \pm 5$      | 0.23                                 |
| O            | Augenbründl                  | $(2.75 \pm 0.42) \cdot 10^{-7}$ | 4.314      | $49 \pm 7$      | 0.19                                 |
| P            | Kamp                         | $(7.02 \pm 1.28) \cdot 10^{-8}$ | 4.997      | $23 \pm 2$      | 0.40                                 |
| Q            | Kaltenbach                   | $(1.86 \pm 0.14) \cdot 10^{-7}$ | 2.431      | $53 \pm 5$      | 0.91                                 |
| R            | Feistritz                    | $(5.65 \pm 1.81) \cdot 10^{-7}$ | 1.431      | $77 \pm 7$      | 0.19                                 |
| S            | Tributary to Reithbach       | $(5.72 \pm 0.30) \cdot 10^{-8}$ | 5.398      | $49 \pm 4$      | 1.11                                 |
| T            | Reithbach                    | $(9.98 \pm 1.23) \cdot 10^{-9}$ | 5.29       | $93 \pm 8$      | 0.80                                 |
| U            | Small tributary to Reithbach | $(3.58 \pm 0.21) \cdot 10^{-8}$ | 1.496      | $88 \pm 12$     | 4.48                                 |
| V            | Kamegg4                      | $(1.24 \pm 0.04) \cdot 10^{-7}$ | 5.416      | $25 \pm 3$      | 6.85                                 |

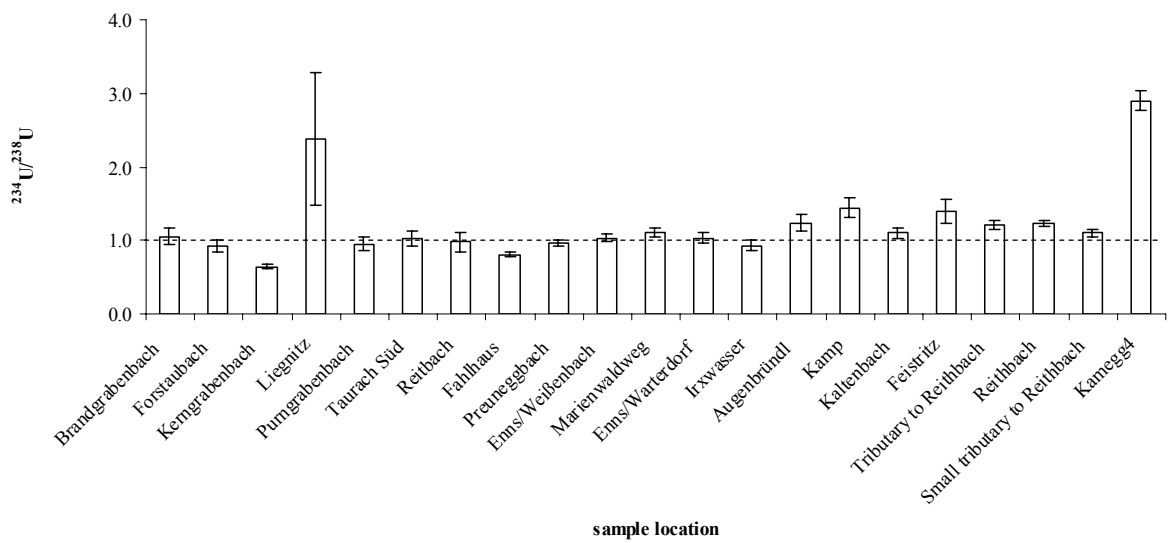
### 3.2.1 Supplementary investigations

Additionally to the already published  $^{236}\text{U}/^{238}\text{U}$  ratios in Austrian water samples, a few other samples were investigated. In Slovakia (Figure 6) water was collected from Prievidza (well, creek and tap water), Žilkovce (tap and creek water), Nove Zamky, Vel'ká Čausa (well water at both locations) and from Budis river. In Slovenia three samples were taken (one river and two sparkling waters) and finally some additional water samples from Austria were measured.



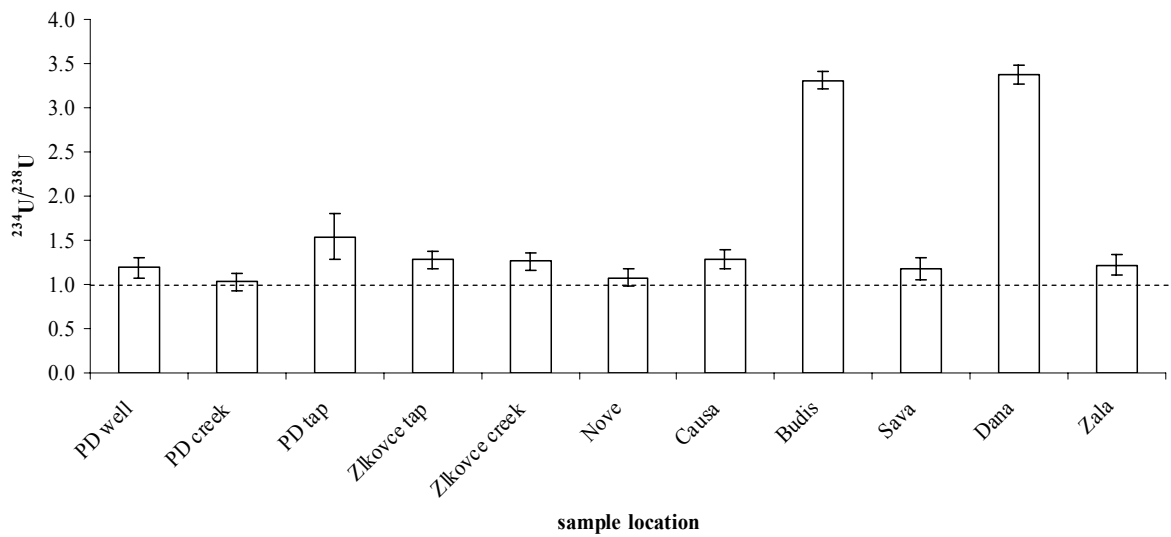
**Figure 6.** Modified map of Slovakia (source: <http://maps.google.at>). Sample sites are indicated by numbers and cycles, respectively.

The chemical separation of uranium by using UTEVA<sup>®</sup> resin and the preparation for the AMS measurement are described in Srncik et al. [78] and references therein. In the following diagrams (Diagram 1a – 1c) the obtained activity ratios  $^{234}\text{U}/^{238}\text{U}$  for all investigated samples are presented. The measurement errors are given in  $\pm 1\sigma$ . Radioactive disequilibrium was found in many samples and in two samples, namely Liegnitz (rivulet water, Salzburg) and Kamegg4 (well water, Lower Austria) the ratios are much higher than 1 (Diagram 1a).



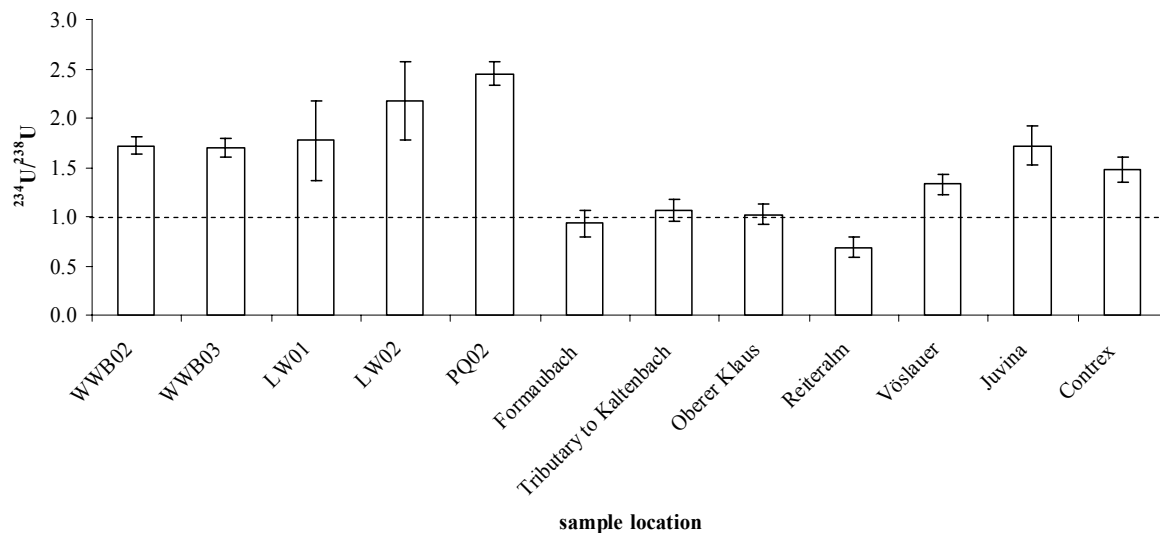
**Diagram 1a.**  $^{234}\text{U}/^{238}\text{U}$  activity ratio of all samples investigated in Srncik et al. [78]

Also the water samples from Slovakia and Slovenia show radioactive disequilibria, especially the Budis and Dana sample (Diagram 1b).



**Diagram 1b.**  $^{234}\text{U}/^{238}\text{U}$  activity ratio of Slovakian and Slovenian water samples. PD stands for Prievidza.

In Diagram 1c only four samples are in radioactive equilibrium; the others show values clearly larger than one.



**Diagram 1c.**  $^{234}\text{U}/^{238}\text{U}$  activity ratio from further Austrian water samples and sparkling waters [Vöslauer (AT), Juvina (AT) and Contrex (F)]

The activity ratio  $^{234}\text{U}/^{238}\text{U}$  was determined in water samples and in most of them a radioactive dis-equilibrium was identified which arises from preferential leaching of  $^{234}\text{U}$  from the soil/rock matrix. The recoil of the  $\alpha$ -decay ( $\sim 10^5$  eV) dislocates the  $^{234}\text{U}$  atom from the lattice, which increases its mobility [79]. So, chemical weathering and the water/rock interactions will lead both to uranium dissolution in the aqueous phase and to  $^{234}\text{U}/^{238}\text{U}$  disequilibrium.

In the following tables the  $^{236}\text{U}/^{238}\text{U}$  results of the water samples are presented; they are grouped per location.

**Table 9.**  $^{236}\text{U}/^{238}\text{U}$  results from Slovakia. Measurement uncertainty is given in  $\pm 1\sigma$ .

| Nr. | Sample        | $^{236}\text{U}/^{238}\text{U}$  | Location     |
|-----|---------------|----------------------------------|--------------|
| 1   | PD well       | $(1.09 \pm 0.13) \times 10^{-7}$ | Prievidza    |
| 1   | PD tap        | $(1.38 \pm 0.81) \times 10^{-7}$ | Prievidza    |
| 1   | PD creek      | $(3.05 \pm 0.03) \times 10^{-7}$ | Prievidza    |
| 2   | Žlkovce tap   | $(2.62 \pm 0.15) \times 10^{-9}$ | Žlkovce      |
| 2   | Žlkovce creek | $(2.39 \pm 0.02) \times 10^{-7}$ | Žlkovce      |
| 3   | Nove          | $(2.04 \pm 0.04) \times 10^{-9}$ | Nove Zamky   |
| 4   | Causa         | $(1.36 \pm 0.07) \times 10^{-8}$ | Vel'ká Čausa |
| 5   | Budis         | $(5.73 \pm 0.19) \times 10^{-9}$ | Budis        |

In Prievidza well, creek and tap water were analysed and they have all an isotopic ratio of few parts in  $10^{-7}$ . The well and tap water are from the same reservoir and they are consistent within  $1\sigma$ . These values are a little bit smaller than for the creek water. The obtained ratios of  $10^{-7}$  are unexpected high and due to no further sampling information the origin of the anthropogenic contribution is unknown but there is no nuclear power plant in the surrounding area.

In the next town (Žlkovce, see Figure 7) tap and creek water were analysed, here no correlation can be seen. The value for the creek is in the same order of magnitude like the creek from Prievidza but the tap water shows a clearly lower value (two orders of magnitude). The sampling collection of the creek water was carried out around 5 km away from the Bohunice nuclear power plant. This could maybe be an explanation for the higher ratio.

In the other three towns (Nove Zamky, Vel'ká Čausa and Budis) the values are between  $10^{-9}$  and  $10^{-8}$ .



**Figure 7.** Žilkovce (source: <http://mapy.atlas.sk>).

The black dot represents the sampling location for the creek water and NPP stands for Nuclear Power Plant.

**Table 10.**  $^{236}\text{U}/^{238}\text{U}$  ( $\pm 1\sigma$ ) results from Slovenia

| Sample | $^{236}\text{U}/^{238}\text{U}$  | Notes           |
|--------|----------------------------------|-----------------|
| Sava   | $(1.22 \pm 0.18) \times 10^{-8}$ | river           |
| Dana   | $(8.07 \pm 3.56) \times 10^{-9}$ | sparkling water |
| Zala   | $(1.06 \pm 0.14) \times 10^{-8}$ | sparkling water |

The samples Sava and Zala show the same isotopic ratio. Dana has a rather untypical large error for AMS measurements.

**Table 11.**  $^{236}\text{U}/^{238}\text{U}$  results for surface and tap water from Austria. PQ02, Vöslauer, Juvina and Contrex are sparkling waters available in the supermarket. Measurement uncertainty is given in  $\pm 1\sigma$ .

| Sample                  | $^{236}\text{U}/^{238}\text{U}$  | Notes                  |
|-------------------------|----------------------------------|------------------------|
| WWB02                   | $(6.44 \pm 0.66) \times 10^{-9}$ | 25 L, Vienna tap water |
| WWB03                   | $(6.76 \pm 0.92) \times 10^{-9}$ | 25 L, Vienna tap water |
| LW01                    | $(9.90 \pm 1.87) \times 10^{-9}$ | 44 L, Vienna tap water |
| LW02                    | $(4.16 \pm 2.33) \times 10^{-9}$ | 31 L, Vienna tap water |
| PQ02                    | $(3.24 \pm 0.47) \times 10^{-8}$ | 25 L, Peterquelle      |
| Formaubach              | $(1.87 \pm 0.62) \times 10^{-9}$ | 25 L, river water      |
| Tributary to Kaltenbach | $(5.39 \pm 0.98) \times 10^{-9}$ | 25 L, river water      |
| Oberer Klaus            | $(3.85 \pm 0.17) \times 10^{-9}$ | 5 L, river water       |
| Reiteralm               | $(1.09 \pm 0.04) \times 10^{-9}$ | 5 L, river water       |
| Vöslauer (AT)           | $(2.47 \pm 0.29) \times 10^{-9}$ | 1.5 L, sparkling water |
| Juvina (AT)             | $(4.18 \pm 0.62) \times 10^{-8}$ | 1.5 L, sparkling water |
| Contrex (F)             | $(4.87 \pm 0.89) \times 10^{-9}$ | 1.5 L, sparkling water |

LW and WWB is the sample code for Vienna tap water. The LW samples were prepared according to the Dowex 1x2 procedure [49] and the WWB samples using the UTEVA<sup>®</sup> resin described in Srncik et al. [78]. The average ratio including all analysed Vienna tap water samples is  $(6.82 \pm 0.80) \times 10^{-9}$ .

In conclusion the  $^{236}\text{U}/^{238}\text{U}$  isotopic ratios in the investigated natural water samples were in the range of  $10^{-7}$  to  $10^{-9}$ . Few parts in  $10^{-9}$  seem to be the lowest possible value for the U isotopic ratio in natural water samples, with the exception of the Gasteiner water which has shown an  $^{236}\text{U}/^{238}\text{U}$  ratio of  $\sim 6.6 \times 10^{-12}$  [20]. In none of the investigated water samples during this study, except the Gasteiner water, a natural  $^{236}\text{U}/^{238}\text{U}$  isotopic ratio below  $10^{-10}$  could be found. It seems that we see a  $^{236}\text{U}$  contamination from global fallout and/or Chernobyl; the origin of the  $^{236}\text{U}$  in mineral waters from deep drilled wells might be a natural one due to the bed-rock of the aquifer.

***Depth profile of  $^{236}\text{U}/^{238}\text{U}$  in soil samples  
in La Palma, Canary Islands***

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### 3.3 Depth profile of $^{236}\text{U}/^{238}\text{U}$ in soil samples in La Palma, Canary Islands

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#### ABSTRACT

The vertical distribution of the  $^{236}\text{U}/^{238}\text{U}$  isotopic ratio was investigated in soil samples from three different locations on La Palma (one of the seven Canary Islands, Spain). Additionally the  $^{240}\text{Pu}/^{239}\text{Pu}$  atomic ratio, as it is a well established tool for the source identification, was determined. The radiochemical procedure consisted of a U separation step by extraction chromatography using UTEVA<sup>®</sup> Resin (Eichrom Technologies, Inc.). Afterwards Pu was separated from Th and Np by anion exchange using Dowex 1x2 (Dow Chemical Co.). Furthermore a new chemical procedure with tandem columns to separate Pu and U from the matrix was tested. For the determination of the uranium and plutonium isotopes by alpha spectrometry thin sources were prepared by microprecipitation techniques. Additionally these fractions separated from the soil samples were measured by Accelerator Mass Spectrometry (AMS) to get information on the isotopic ratios  $^{236}\text{U}/^{238}\text{U}$ ,  $^{240}\text{Pu}/^{239}\text{Pu}$  and  $^{236}\text{U}/^{239}\text{Pu}$ , respectively. The  $^{236}\text{U}$  concentrations [atoms/g] in each surface layer (~2 cm) were surprisingly high compared to deeper layers where values around two orders of magnitude smaller were found. Since the isotopic ratio  $^{240}\text{Pu}/^{239}\text{Pu}$  indicated a global fallout signature we assume the same origin as the probable source for  $^{236}\text{U}$ . Our measured  $^{236}\text{U}/^{239}\text{Pu}$  value of around 0.2 is within the expected range for this contamination source.

Keywords: soil samples; global fallout;  $^{236}\text{U}/^{238}\text{U}$ ;  $^{240}\text{Pu}/^{239}\text{Pu}$ ;  $^{236}\text{U}/^{239}\text{Pu}$

## 1. Introduction

The major source of actinides (as e.g. plutonium) in the environment is global fallout which arose from about 541 atmospheric nuclear explosions (UNSCEAR Report, 1993). Other sources are nuclear reactor accidents (Chernobyl), discharges of radioactive waste (Sellafield, La Hague, Mayak) and accidents with nuclear devices (e.g. Palomares, Thule) (Salbu, 2001). Soil samples from three different locations on La Palma, Canary Islands, (see Figure 1) were collected in November 2007 and in February 2009. The emphasis on this work was the vertical distribution of  $^{236}\text{U}/^{238}\text{U}$  in the soil and the measurement of Pu. In addition the determination of the  $^{236}\text{U}/^{239}\text{Pu}$  isotopic ratio in these samples was carried out.

$^{236}\text{U}$  with a half life of  $2.3 \times 10^7$  years is continuously produced by thermal neutron capture on  $^{235}\text{U}$  which is omnipresent in the environment. The natural  $^{236}\text{U}$  production results from neutrons produced by ( $\alpha$ ,n)-reactions on lighter nuclides (e.g. Na and Mg), spontaneous fission of  $^{238}\text{U}$ , induced fission of  $^{235}\text{U}$  and at the earth's surface from cosmic rays (Wilcken et al., 2008). A  $^{236}\text{U}/^{238}\text{U}$  isotopic ratio between  $1 \times 10^{-14}$  and  $5 \times 10^{-14}$  can be expected for typical crustal rocks with a uranium and thorium content of a few ppm (Steier et al., 2008). On the other hand, significant releases to the environment can be expected as  $^{236}\text{U}$  is a by-product in nuclear power plants. This potentially enhances the very low natural isotopic ratio, but the environmental distribution of anthropogenic  $^{236}\text{U}$  is not well investigated yet. The present work is part of a larger effort to assess the dispersion of anthropogenic  $^{236}\text{U}$  in different compartments of the environment. The summit of La Palma Island is chosen since it allows relatively easy access to a site with clean tropospheric air, far away from anthropogenic emissions. It is thus well suited for studying fallout at minimum risk of local contamination. The climate of the Canary Islands (Herrera et al., 2001) is dominated by the direct influence of the trade wind belt, which blows mainly against the northern of the islands. La Palma (2312 m a.s.l.) is the second highest island of the Canary archipelago, and the most humid ( $\sim 1000$  mm/year at the sampling sites). The exceptional steep topography of La Palma leads to condensation directly from high-altitude clean air. Since the deposition of global fallout is controlled by precipitation, a sufficient amount of radionuclides is expected. On the other hand, the high mountain ranges of La Palma are easily accessible on good roads, since they host several European astronomical observatories.

Measurements of  $^{236}\text{U}$  became possible only recently by AMS on very few facilities, as e.g. VERA (Vienna Environmental Research Accelerator); plutonium isotopes, on the contrary, are comparably well studied as tracer for anthropogenic actinides with alpha spectrometry and

ICP-MS (Ketterer and Szechenyi, 2008) but also by AMS (Oughton and Fifield, 2001). Although the environmental behaviour of U and Pu differs significantly, we consider plutonium as the best candidate for a methodical comparison. Also for Pu, AMS seems to have the best overall sensitivity (Fifield, 2008) but it can also be measured by other mass spectrometric techniques with partially higher detection efficiency (Steier et al., 2010). Recently soil samples from a site which was solely influenced by global fallout could be investigated for their  $^{236}\text{U}$  concentration. The amount ranged from  $10^8 - 10^9$  atoms/g dry soil (Sakaguchi et al., 2009). A constant  $^{236}\text{U}/^{239}\text{Pu}$  ratio of  $\sim 0.2$  was found, which was interpreted as the original fingerprint of global fallout. In the general environment, however, differences in the mobility of Pu and U will lead to deviations from this ratio.

In this paper the combined procedure for the determination of U and Pu in soil samples is presented. Two column chromatography methods were applied: at the beginning the sample solution was passed through a column filled with UTEVA<sup>®</sup> Resin (Eichrom Technologies, Inc.) to separate U, and then the Pu fraction was purified with a second anion exchange step by using Dowex 1x2 (100-200 mesh, Dow Chemical Co.). The second method consisted of a double column system. The first column was filled with Dowex 1x8 and the second one with UTEVA<sup>®</sup> Resin. The UTEVA column was placed directly below the anion exchange column. The advantage of this method is that no further purification (i.e. additional column chromatography steps) of the Pu fraction was necessary.

We present first  $^{236}\text{U}/^{238}\text{U}$  ratios from a clean-air area as well as  $^{240}\text{Pu}/^{239}\text{Pu}$  and  $^{236}\text{U}/^{239}\text{Pu}$  atomic ratios, from which the contamination source (namely global fallout) can be derived.

## 2. Materials and methods

The samples were collected at three different sites on the island La Palma in the Atlantic Ocean. Despite samples were taken close to roads or trails, we looked out for an intact and site-typical vegetation cover as indication for the absence of anthropogenic disturbance. From the first sampling location (N 28° 45.233' / W 17° 53.421', 2330 m a.s.l.) on the northern slope of Roque de los Muchachos two cores (IA and IB) were available which were separated into 2 cm layers and stored in plastic bags. The full length was 10 cm and 12 cm for IA and IB, respectively. At the second site several 100 m downhill (N 28° 46.191' / W 17° 54.224', 1970 m a.s.l.) again two cores with 8 cm length were collected (IIC and IID). IIC was separated into 2 cm layers whereas IID was taken as a bulk sample. Two years later two additional bulk samples (LP\_B1 and LP\_B2) were collected from the same site as IIC and

IID: the depth of LP\_B1 ranged from 0 to 5 cm. LP\_B2 was sampled from an outcrop apparently exposed by road construction between 2007 and 2009. Approximately 10 cm of the vertical surface of the outcrop were removed, and then the material was taken from 15 to 40 cm below the horizontal surface. Additionally a third bulk sample (LP\_A) was collected on Pico de La Nieve (N 28° 43.717' / W 17° 49.636', ~ 2000 m a.s.l) with a depth down to 5 cm. In the time period between the two collection dates the sample procedure was improved. While the samples picked up in 2007 were prepared according to the chemical separation procedure A, the samples taken in 2009 were processed following the faster and more comfortable sample preparation B. The main difference of the second procedure is the usage of UTEVA<sup>®</sup> Resin coupled with Dowex 1x8 but few other changes are in the detail and therefore both sample treatments are described separately below. For spiking a stock solution of <sup>236</sup>Pu was obtained from the University of Helsinki and calibrated against SRM 4334G (<sup>242</sup>Pu solution) by alpha spectrometry. Furthermore a stock solution of SRM 4324B (<sup>232</sup>U solution) was used. One reference sample (IAEA-135, Radionuclides in Irish Sea Sediment) was investigated with respect to Pu and U in order to check the validity of our results.

### *2.1 Chemical separation procedure A*

After drying the samples by air, they were ashed in porcelain crucibles in an electric muffle furnace at 420°C for 24 h. The radiochemical procedure applied to the analysis of U and Pu by alpha spectrometry followed the procedures given in (Eichrom Technologies, 2005; Hrnccek et al., 2002) with slight modifications which are discussed briefly below. Between 5 and 20 g soil were leached in 100 mL 65 % HNO<sub>3</sub> and 25 mL 37 % HCl, 0.5 g NaNO<sub>2</sub>, <sup>236</sup>Pu and <sup>232</sup>U tracer solutions were added. After boiling the mixture for 3 h, the sample was centrifuged for 30 min at 4 000 rpm (relative centrifugal force (RCF) is 1646). The soil residue was leached twice with 20 mL 65 % HNO<sub>3</sub> and 15 mL 48 % HF for 1 h and was then rejected. The supernatant solutions were combined and evaporated to near dryness. The residue was fumed twice with 10 mL boric acid (c = 5g/100ml), three times with 10 mL 65 % HNO<sub>3</sub> and 4 mL 32 % H<sub>2</sub>O<sub>2</sub>. The residue was taken up in 20 mL 3M HNO<sub>3</sub> – 1M Al(NO<sub>3</sub>)<sub>3</sub> and insoluble particles were removed by centrifugation.

#### *2.1.1 Separation of uranium*

0.5 g UTEVA<sup>®</sup> resin was preconditioned with 3M HNO<sub>3</sub>, the sample solution was brought onto the column which was then washed with 35 mL 3M HNO<sub>3</sub>. Pu was eluted with 10 mL

9M HCl and 30 mL 5M HCl – 0.05M oxalic acid, and finally U was eluted with 30 mL 1M HCl.

### *2.1.2 Purification of plutonium*

The solution containing Pu was taken to dryness and fumed three times with 5 mL 65 % HNO<sub>3</sub> and 2 mL 32 % H<sub>2</sub>O<sub>2</sub>. The residue was taken up with 20 mL 1M HNO<sub>3</sub> and 100 mg Mohr's salt [(NH<sub>4</sub>)<sub>2</sub>Fe(SO<sub>4</sub>)x6H<sub>2</sub>O] were added to reduce Pu to trivalent state. Afterwards the solution was adjusted to 8M HNO<sub>3</sub> by adding 20 mL 65 % HNO<sub>3</sub>. Finally Pu was oxidized to tetravalent oxidation state by addition of 0.5 g NaNO<sub>2</sub>. The excess of nitrous acid was destroyed by gently boiling (NO<sub>x</sub> fumes). 6g Dowex 1x2 were preconditioned with 8M HNO<sub>3</sub> and then the sample solution was loaded onto the column which was subsequently washed with 50 mL 8M HNO<sub>3</sub>. Th was removed with 30 mL 37 % HCl and Pu was eluted with 50 mL 0.36M HCl – 0.014M HF.

The U and Pu fractions were evaporated until dryness and fumed three times with 5 mL 65 % HNO<sub>3</sub> and 2 mL 32 % H<sub>2</sub>O<sub>2</sub>. The U fraction was additionally fumed with 37 % HCl (3x). Afterwards the Pu was dissolved in 20 mL 1M HNO<sub>3</sub> and U in 20 mL 1M HCl to carry out the microprecipitation (description see 2.3) for the alpha source preparation.

### *2.2 Chemical separation procedure B*

The procedure described below (modified from Eichrom Technologies, 2005; Moreno et al., 1997; Warneke et al., 2002) was used for the bulk samples collected in 2009. Samples of 20 g were dried in an electric oven at 100°C to constant weight and afterwards ashed in porcelain crucibles in an electric muffle furnace at 420°C for 24 h. The sample was transferred to a Teflon beaker and was leached according to 2.1 “Chemical separation procedure A”. Afterwards the combined solutions were evaporated till dryness, fumed three times with 10 mL boric acid (c = 5 g/100 mL), with 10 mL 37 % HCl (3x) and with 10 mL 65 % HNO<sub>3</sub> (3x). The residue was dissolved in 8M HNO<sub>3</sub> and a redox adjustment of Pu was carried out as described in section 2.1. The insoluble part was removed by centrifugation (5 min at 4000 rpm). Two columns were prepared; the first one was filled with 6 g Dowex 1x8 (100-200 mesh, Dow Chemical Co.) and the second column with 0.5 g UTEVA<sup>®</sup> (Eichrom Technologies, Inc.). The UTEVA<sup>®</sup> column was placed directly under the anion exchange column and both were pre-conditioned with 8M HNO<sub>3</sub>. The sample solution was transferred to the Dowex 1x8 column and the eluent passed directly onto the UTEVA<sup>®</sup> column. After

washing with 60 ml 8M HNO<sub>3</sub> the columns were separated. The Dowex 1x8 column was washed with 50 mL 37 % HCl to remove Th, and Pu was finally eluted with 50 mL 0.1M NH<sub>4</sub>I – 9M HCl. The iodide reduced Pu(IV) to Pu(III) which does not form chloride complexes and was no longer retained by the column. The UTEVA<sup>®</sup> resin was washed with 40 mL 3M HNO<sub>3</sub>, traces of Th and Np were eluted with 10 mL 9M HCl and 30 mL 5M HCl – 0.05M oxalic acid. Finally U was eluted with 30 mL 1M HCl. The U and Pu fractions were treated according the last paragraph in section 2.1.2.

### 2.3 Microprecipitation

To the plutonium fraction a tip of a spatula of Mohr's salt, 0.5 mL of a 25% NaNO<sub>2</sub> solution and 50 µL of a Nd<sup>3+</sup>-solution (c = 1mg/mL) were added.

To the U fraction 50 µL of a Nd<sup>3+</sup>-solution (c = 1 mg/mL) were added and U was reduced to tetravalent oxidation state by addition of 100 µL 15% TiCl<sub>3</sub>-solution. Afterwards 5 mL 40% HF were added to both of the solutions. After 1h the samples were filtered through a cellulose nitrate membrane filter (Whatman<sup>®</sup>, 0.1 µm pore size), washed three times with 2 mL 4% HF and twice with 2 mL Millipore water (18.2 MΩ·cm).

### 2.4 Alpha measurement

Alpha spectrometry was performed with a PIPS (Passivated Implanted Planar Silicon) Detector, Model 7401 VR, Canberra/Packard with an active area of 450 mm<sup>2</sup>. The counting time was 252 000 s and 604 800 s for U and Pu, respectively. For these measurements, the detection limits calculated according to Currie (1968) were 1.12 mBq/sample for <sup>238</sup>U and 0.80 mBq/sample for <sup>239(40)</sup>Pu. The software Genie 2.1 (Canberra, USA) was used for the evaluation of the spectra.

### 2.5 AMS measurement

The filters already analysed by alpha spectrometry were reprocessed for the AMS measurement according to Srncik et al. (2008). The filters were dissolved in HNO<sub>3</sub>, the nuclides of interest were co-precipitated with iron hydroxide, and combusted to oxides which are pressed into an aluminium sample holder either with or without silver as binder. The VERA setup as used for actinide measurements is described in Vockenhuber et al. (2003) and Steier et al. (2010).

$\text{PuO}^-$  at 50 keV was produced in a Cs-sputter source, mass analyzed, accelerated to 3 MeV and stripped to positive charge state in a gas cell. By these means, all interfering molecular isobars are destroyed. The 5+ charge state is selected in a second, high energy mass spectrometer, after acceleration to 18 MeV. A combination of an ionization chamber and a time-of-flight measurement allow a unique identification of the isotope of interest. Significant background exists for  $^{240}\text{Pu}^{5+}$ , apparently from stable  $^{144}\text{Nd}^{3+}$ , which shares the same mass-to-charge ratio and thus cannot be suppressed by the mass spectrometer. In the present measurement, the residual Nd concentration in the sputter samples was, however, low enough and could therefore be separated in the energy-resolving detector.

The machine was tuned with  $^{238}\text{U}^{16}\text{O}^-$  as a pilot beam, and the parameters were then scaled to the different rare radioisotopes which do not provide sufficient beam current for tuning. Alternating measurements of  $^{239}\text{Pu}$  and  $^{240}\text{Pu}$  were performed, with duration of several 100 s each. By these means, one tries to minimize the impact of source output variations on the measured count rate results. For  $^{236}\text{U}$ ,  $^{238}\text{U}^{16}\text{O}^-$  can be measured once per second as a current before the accelerator, which renders source output variations negligible. Our in-house standard Vienna-KkU,  $^{236}\text{U}/\text{U} = (6.98 \pm 0.32) \times 10^{-11}$  (Steier et al., 2008) was used to normalize the  $^{236}\text{U}$  measurements. However, no standard is available for Pu; this introduces an additional uncertainty, which is however expected to be in the range of a few percent. Measurement times per sample ranged from 30 min to several hours, depending mainly on the machine time availability. Generally, the prepared samples last for several hours, and an efficiency of  $\sim 10^{-4}$  (counts in the detector per atom in sputter sample) is achieved if the samples are completely sputtered.

### 3. Results and discussion

The chemical separation A has been already applied in our laboratory but for sample preparation B the validity was checked by analysing an IAEA-135 reference material. The obtained result was  $(225 \pm 7)$  Bq/kg  $^{239(40)}\text{Pu}$ ; this value is in good agreement with the recommended value of  $(205 - 226)$  Bq/kg for  $^{239(40)}\text{Pu}$ . The IAEA-135 standard was also measured for its  $^{236}\text{U}/^{238}\text{U}$  ratio by AMS. Our value of  $(1.48 \pm 0.04) \times 10^{-6}$  agrees with Hotchkis et al. (2000) who determined  $(1.48 \pm 0.37) \times 10^{-6}$  via AMS. Our result indicated a very good accuracy of the proposed method.

In Table 1 the results of the  $^{236}\text{U}/^{238}\text{U}$  isotopic ratios and  $^{236}\text{U}$  [atoms/g] for all core layers and also for the bulk samples are shown. In each core (IA, IB and IID) the main amount of  $^{236}\text{U}$

was found in the surface layer (between  $10^9$  and  $10^{10}$  atoms/g dry soil). With increasing depth the number of atoms per gram measured was in the range of  $10^7$ , except for the depth profile of IA. Here again an increase of two orders of magnitude was obtained for the deepest layer. As this value is so high and therefore implausible, we assume that a mistake during the sample collection occurred. According to the results that a relatively high value of  $^{236}\text{U}$  atoms/g in each surface layer was found in contrast to the deeper layers (decrease by two orders of magnitude), it seems that the anthropogenic  $^{236}\text{U}$  was not moving downwards. The layers below the “surface layer” show at all sites (IA, IB and IID) at least the same order of magnitude of  $^{236}\text{U}$  atoms/g. The result of the respective subsamples of LP\_B1 and LP\_B2 are consistent with the exception of LP\_B2\_2 which was below the blank value. The result of sample LP\_A\_2 is higher but agrees with LP\_A\_1 and LP\_A\_3 within  $2\sigma$ . Both bulk samples LP\_B1 (0-5 cm) and LP\_B2 (15-40 cm) show a  $^{236}\text{U}$  concentration in the range of  $10^8$  atoms/g dry soil. For the LP\_A bulk sample (0-5 cm depth) the results are one order of magnitude higher which reflects inhomogeneities in the  $^{236}\text{U}$  distribution at different sample sites.

The isotopic ratios  $^{236}\text{U}/^{238}\text{U}$  ranged from  $10^{-7}$  near the surface to  $10^{-9}$  with increasing depth. The obtained ratios of  $10^{-9}$  are not influenced by our blanks; this was proven by a blank correction. At the sample location LP\_B1, (0-5 cm) the level of few parts in  $10^{-8}$  was found and at LP\_B2 (15-40 cm) the isotopic ratio is one order of magnitude lower. The value for LP\_A is slightly higher than the bulk samples at the LP\_B site.

Table 2 shows the vertical distribution of  $^{239(40)}\text{Pu}$  [Bq/kg] for each of the three sample locations (cores IA, IB and IID). At the sample site IA the surface layer (0-2 cm) got lost. The specific activities of  $^{239(40)}\text{Pu}$  in layer LP01a (2-6 cm) and LP02a (6-8 cm) at location IA are similar  $[(0.32 \pm 0.05) \text{ Bq/kg}$  and  $(0.35 \pm 0.06) \text{ Bq/kg}$ , respectively]; in the deepest layer a decrease of one order of magnitude occurred. The highest specific activity at location IB of  $(0.46 \pm 0.03) \text{ Bq/kg}$  was found in the surface layer (0-2 cm). The values for LP05a (2-4 cm) and LP09 (10-12 cm) were below the limit of detection ( $< 0.040 \text{ Bq/kg}$ ). At the sample location IID the highest value occurred in the layer between 2-4 cm and the decrease of the activity is less marked than at the other two locations. Also here two samples, LP12a (4-6 cm) and LP14 (8-10 cm), were below the detection limit ( $< 0.080 \text{ Bq/kg}$ ).

The accumulated levels at site IB and IID were  $(36 \pm 11) \text{ Bq } ^{239(40)}\text{Pu m}^{-2}$  and  $(22 \pm 7) \text{ Bq } ^{239(40)}\text{Pu m}^{-2}$ , respectively. These  $^{239(40)}\text{Pu}$  results are in the range of the expected value  $[(36 \pm$

3) Bq  $^{239(40)}\text{Pu m}^{-2}$ ] for global fallout in the Northern Hemisphere at latitude 20° to 30° N (Hardy et al., 1973).

Buesseler (1997) reports for the global fallout  $^{240}\text{Pu}/^{239}\text{Pu}$  isotopic ratio a typical interval of 0.175 – 0.19. According to Kelley et al. (1999) the average composition of fallout  $^{240}\text{Pu}/^{239}\text{Pu}$  for the north equatorial region (latitude, 30°N-0) is 0.178 with a standard deviation of 0.019 ( $2\sigma$ ). The ratio for Chernobyl is 0.45 – 0.52 (Kutkov et al., 1995).

In the present work, for some samples the  $^{240}\text{Pu}/^{239}\text{Pu}$  ratio could not be determined (indicated by “-“ in Table 3) due to relatively small  $^{239}\text{Pu}$  and  $^{240}\text{Pu}$  count rates. One reason was the low Pu chemical yield (the average was  $24.3 \pm 0.7$ ) determined by alpha spectrometry which is attributed to difficulties during the leaching and fuming steps before the column separation step. Additionally, sometimes problems during the  $\text{Fe}(\text{OH})_3$  co-precipitation occurred which would further explain losses of Pu and therefore the low count rate by AMS. From Table 3 it can be seen that at the sample location IA only the first layer could be measured and is in agreement with global fallout, although the value was slightly higher. The  $^{240}\text{Pu}$  count rates of both LP02a (6-8 cm) and LP03 (8-10 cm) were too low to determine the  $^{240}\text{Pu}/^{239}\text{Pu}$  isotopic ratio. The  $^{240}\text{Pu}/^{239}\text{Pu}$  results in all layers of location IB and IID showed a ratio indicating global fallout. The average isotopic ratio of bulk sample LP\_B1 was  $0.221 \pm 0.029$ . For all three sub-samples of LP\_B2 (15-40 cm below the surface)  $^{239}\text{Pu}$  was far below the blank value and therefore no atomic ratio could be determined. The mean  $^{240}\text{Pu}/^{239}\text{Pu}$  ratio of bulk sample LP\_A was  $0.287 \pm 0.025$  which is slightly higher than the expected value for global fallout.

Table 4 shows the  $^{236}\text{U}/^{239}\text{Pu}$  results for all layers and bulk samples, respectively. According to the isotopic ratios of  $^{240}\text{Pu}/^{239}\text{Pu}$  found in the La Palma soil samples (Table 3), the source of contamination seems to be global fallout. Ketterer et al. (2007) reported  $^{236}\text{U}/^{239}\text{Pu}$  atomic ratios between 0.05 and 0.5 for samples containing Pu of purely stratospheric fallout. The wide range was attributed to the evidently higher mobility of fallout  $^{236}\text{U}$  compared to Pu (Ketterer et al., 2007). However, this migration behaviour of U and Pu was not observed by Sakaguchi et al. (2009), who investigated at three sites 20 m apart from each other soil samples (0-30 cm) from Ishikawa Prefecture (Japan); here the  $^{236}\text{U}/^{239}\text{Pu}$  isotopic ratios were in the much smaller range of 0.212 to 0.253. In our work (compare Table 1 and 2) the overwhelming part of  $^{236}\text{U}$  in the core samples was found in the surface layers, while the (unfortunately sparse) Pu data indicates a more even distribution. Consequently, the three topmost samples reveal an enhanced  $^{236}\text{U}/^{239}\text{Pu}$  ratio higher than 3. All other values are in the

range supposed by Ketterer et al. (2007) and for the bulk sub-samples LP\_B1 (0-5 cm) a  $^{236}\text{U}/^{239}\text{Pu}$  value of 0.2 similar to the bulk samples of Sakaguchi et al. (2009) was found. We obtained for the bulk sample LP\_A (0-5 cm) a higher average ratio ( $^{236}\text{U}/^{239}\text{Pu} = 0.5$ ) but with a larger scatter between sub-samples.

#### 4. Conclusion

Soil samples from a remote clean air site, the La Palma Island, were investigated with the emphasis on the  $^{236}\text{U}/^{238}\text{U}$  ratio. A conventional and a new tandem column procedure were applied for the sequential and simultaneous separation of U and Pu, respectively. Samples were measured both by alpha spectrometry and AMS. The isotopic ratio of  $^{236}\text{U}/^{238}\text{U}$  was between  $10^{-7}$  for the surface samples and  $10^{-9}$  for deeper layers. The  $^{236}\text{U}$  [atoms/g] results at each surface layer were surprisingly high and the decrease to deeper layers were around two orders of magnitude; this phenomenon was not observed for Pu. The isotopic ratio  $^{240}\text{Pu}/^{239}\text{Pu}$  is a well established indicator for the identification of the contamination source. In our samples the  $^{240}\text{Pu}/^{239}\text{Pu}$  atom ratios of 0.149 - 0.267 for site IA, IB and IID indicate that global fallout is the probable source for the Pu isotopes similarly to site LP\_B1 where the mean isotopic ratio is  $0.221 \pm 0.029$ . In accordance with the  $^{240}\text{Pu}/^{239}\text{Pu}$  results, most of our measured  $^{236}\text{U}/^{239}\text{Pu}$  isotopic ratios were in the order of 0.04 and 0.78 and agree with the sparse set of already published values for the global fallout signature.

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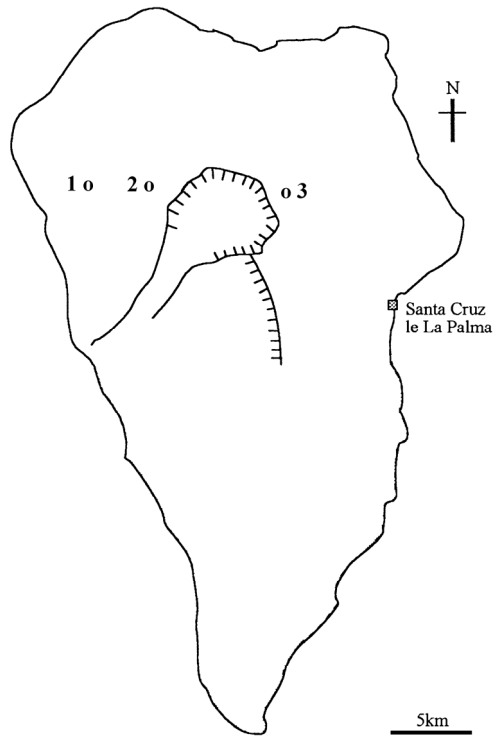
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**Figure captions**

**Fig. 1.** Modified map from La Palma (Moss et al., 1999). The numbers with the respective cycles indicate the sampling sites (1 represents IIC, IID and LP\_B1, LP\_B2, number 2 stands for IA, IB and 3 for LP\_A).



### Tables and diagrams

**Table 1** Results of the isotopic ratio  $^{236}\text{U}/^{238}\text{U}$  and  $^{236}\text{U}$  [atoms/g] in soil samples from La Palma. The measurement uncertainties are given in  $\pm 1\sigma$ .

#### Depth profile - IA

| Sample | Core, depth [cm] | $^{236}\text{U}/^{238}\text{U}$  | $^{236}\text{U}$ [atoms/g]    |
|--------|------------------|----------------------------------|-------------------------------|
| LP01a  | IA, 2 - 6        | $(2.37 \pm 0.07) \times 10^{-7}$ | $(9.69 \pm 1.62) \times 10^9$ |
| LP02a  | IA, 6 - 8        | $(2.96 \pm 0.20) \times 10^{-9}$ | $(6.08 \pm 0.73) \times 10^7$ |
| LP03   | IA, 8 - 10       | $(1.23 \pm 0.04) \times 10^{-7}$ | $(1.93 \pm 0.31) \times 10^9$ |

#### Depth profile - IB

| Sample | Core, depth [cm] | $^{236}\text{U}/^{238}\text{U}$  | $^{236}\text{U}$ [atoms/g]    |
|--------|------------------|----------------------------------|-------------------------------|
| LP04   | IB, 0 - 2        | $(3.15 \pm 0.09) \times 10^{-7}$ | $(8.76 \pm 1.62) \times 10^9$ |
| LP05a  | IB, 2 - 4        | $(3.01 \pm 0.09) \times 10^{-9}$ | $(3.91 \pm 0.56) \times 10^7$ |
| LP06   | IB, 4 - 6        | $(3.90 \pm 0.21) \times 10^{-9}$ | $(8.12 \pm 1.24) \times 10^7$ |
| LP07   | IB, 6 - 8        | $(2.10 \pm 0.23) \times 10^{-9}$ | $(4.95 \pm 1.12) \times 10^7$ |
| LP08a  | IB, 8 - 10       | $(1.00 \pm 0.11) \times 10^{-9}$ | $(1.43 \pm 0.33) \times 10^7$ |
| LP09   | IB, 10 - 12      | $(2.13 \pm 0.16) \times 10^{-9}$ | $(5.46 \pm 0.89) \times 10^7$ |

#### Depth profile - IID

| Sample | Core, depth [cm] | $^{236}\text{U}/^{238}\text{U}$  | $^{236}\text{U}$ [atoms/g]    |
|--------|------------------|----------------------------------|-------------------------------|
| LP10   | IID, 0 - 2       | $(2.54 \pm 0.08) \times 10^{-7}$ | $(2.82 \pm 0.48) \times 10^9$ |
| LP11   | IID, 2 - 4       | $(4.93 \pm 0.34) \times 10^{-9}$ | $(2.61 \pm 0.48) \times 10^7$ |
| LP12a  | IID, 4 - 6       | $(3.25 \pm 0.16) \times 10^{-9}$ | $(5.64 \pm 0.96) \times 10^7$ |
| LP13   | IID, 6 - 8       | $(3.54 \pm 0.33) \times 10^{-9}$ | $(2.85 \pm 0.49) \times 10^7$ |
| LP14   | IID, 8 - 10      | $(3.52 \pm 0.29) \times 10^{-9}$ | $(4.41 \pm 0.96) \times 10^7$ |

#### IIC bulk sample

| Sample | Core, depth [cm] | $^{236}\text{U}/^{238}\text{U}$  | $^{236}\text{U}$ [atoms/g]    |
|--------|------------------|----------------------------------|-------------------------------|
| LP15a  | IIC, 0 - 8       | $(4.35 \pm 0.24) \times 10^{-9}$ | $(5.75 \pm 1.18) \times 10^7$ |

#### LP\_B1 bulk sample, again from IIC/IID

| Sample  | Depth [cm] | $^{236}\text{U}/^{238}\text{U}$  | $^{236}\text{U}$ [atoms/g]    |
|---------|------------|----------------------------------|-------------------------------|
| LP_B1_1 | 0 - 5      | $(2.36 \pm 0.07) \times 10^{-8}$ | $(4.44 \pm 0.89) \times 10^8$ |
| LP_B1_2 | 0 - 5      | $(2.45 \pm 0.07) \times 10^{-8}$ | $(2.50 \pm 0.41) \times 10^8$ |
| LP_B1_3 | 0 - 5      | $(2.48 \pm 0.07) \times 10^{-8}$ | $(3.22 \pm 0.64) \times 10^8$ |

#### LP\_B2 bulk sample, again from IIC/IID

| Sample  | Depth [cm] | $^{236}\text{U}/^{238}\text{U}$  | $^{236}\text{U}$ [atoms/g]    |
|---------|------------|----------------------------------|-------------------------------|
| LP_B2_1 | 15 - 40    | $(4.85 \pm 1.69) \times 10^{-9}$ | $(2.49 \pm 0.92) \times 10^8$ |
| LP_B2_2 | 15 - 40    | -                                | -                             |
| LP_B2_3 | 15 - 40    | $(3.25 \pm 1.54) \times 10^{-9}$ | $(1.78 \pm 0.88) \times 10^8$ |

#### LP\_A bulk sample

| Sample | Depth [cm] | $^{236}\text{U}/^{238}\text{U}$  | $^{236}\text{U}$ [atoms/g]    |
|--------|------------|----------------------------------|-------------------------------|
| LP_A_1 | 0 - 5      | $(4.21 \pm 0.13) \times 10^{-8}$ | $(4.01 \pm 0.48) \times 10^9$ |
| LP_A_2 | 0 - 5      | $(3.41 \pm 0.35) \times 10^{-8}$ | $(2.20 \pm 0.43) \times 10^9$ |
| LP_A_3 | 0 - 5      | $(1.31 \pm 0.57) \times 10^{-8}$ | $(1.00 \pm 0.46) \times 10^9$ |

**Table 2.** Vertical distribution of  $^{239(40)}\text{Pu}$  [Bq/kg] at the sample location IA, IB and IID and the measurement uncertainty is given  $\pm 1\sigma$ .

Depth profile - IA

| Sample | Depth [cm] | $^{239(40)}\text{Pu}$ [Bq/kg] |
|--------|------------|-------------------------------|
| LP01a  | IA, 2 - 6  | $0.322 \pm 0.045$             |
| LP02a  | IA, 6 - 8  | $0.350 \pm 0.055$             |
| LP03   | IA, 8 - 10 | $0.026 \pm 0.007$             |

Depth profile - IB

| Sample | Depth [cm]  | $^{239(40)}\text{Pu}$ [Bq/kg] |
|--------|-------------|-------------------------------|
| LP04   | IB, 0 - 2   | $0.458 \pm 0.028$             |
| LP05a  | IB, 2 - 4   | -                             |
| LP06   | IB, 4 - 6   | $0.088 \pm 0.010$             |
| LP07   | IB, 6 - 8   | $0.055 \pm 0.011$             |
| LP08a  | IB, 8 - 10  | $0.037 \pm 0.013$             |
| LP09   | IB, 10 - 12 | -                             |

Depth profile - IID

| Sample | Depth [cm]  | $^{239(40)}\text{Pu}$ [Bq/kg] |
|--------|-------------|-------------------------------|
| LP10   | IID, 0 - 2  | $0.296 \pm 0.065$             |
| LP11   | IID, 2 - 4  | $0.601 \pm 0.100$             |
| LP12a  | IID, 4 - 6  | -                             |
| LP13   | IID, 6 - 8  | $0.136 \pm 0.025$             |
| LP14   | IID, 8 - 10 | -                             |

**Table 3** Results of  $^{240}\text{Pu}/^{239}\text{Pu}$  by AMS in soil samples from La Palma. The measurement uncertainties are given in  $\pm 1\sigma$ .

| Depth profile - IA |                  |                                   |
|--------------------|------------------|-----------------------------------|
| Sample             | Core, depth [cm] | $^{240}\text{Pu}/^{239}\text{Pu}$ |
| LP01a              | IA, 2 - 6        | $0.267 \pm 0.056$                 |
| LP02a              | IA, 6 - 8        | -                                 |
| LP03               | IA, 8 - 10       | -                                 |

| Depth profile - IB |                  |                                   |
|--------------------|------------------|-----------------------------------|
| Sample             | Core, depth [cm] | $^{240}\text{Pu}/^{239}\text{Pu}$ |
| LP04               | IB, 0 - 2        | $0.149 \pm 0.006$                 |
| LP05a              | IB, 2 - 4        | $0.178 \pm 0.015$                 |
| LP06               | IB, 4 - 6        | $0.198 \pm 0.050$                 |
| LP07               | IB, 6 - 8        | $0.149 \pm 0.051$                 |
| LP08a              | IB, 8 - 10       | -                                 |
| LP09               | IB, 10 - 12      | -                                 |

| Depth profile - IID |                  |                                   |
|---------------------|------------------|-----------------------------------|
| Sample              | Core, depth [cm] | $^{240}\text{Pu}/^{239}\text{Pu}$ |
| LP10                | IID, 0 - 2       | $0.150 \pm 0.018$                 |
| LP11                | IID, 2 - 4       | $0.195 \pm 0.089$                 |
| LP12a               | IID, 4 - 6       | $0.189 \pm 0.035$                 |
| LP13                | IID, 6 - 8       | -                                 |
| LP14                | IID, 8 - 10      | -                                 |

| IIC bulk sample |                  |                                   |
|-----------------|------------------|-----------------------------------|
| Sample          | Core, depth [cm] | $^{240}\text{Pu}/^{239}\text{Pu}$ |
| LP15a           | IIC, 0 - 8       | $0.131 \pm 0.029$                 |

| LP_B1 bulk sample, again from IIC/IID |            |                                   |
|---------------------------------------|------------|-----------------------------------|
| Sample                                | Depth [cm] | $^{240}\text{Pu}/^{239}\text{Pu}$ |
| LP_B1_1                               | 0 - 5      | $0.251 \pm 0.060$                 |
| LP_B1_2                               | 0 - 5      | $0.198 \pm 0.027$                 |
| LP_B1_3                               | 0 - 5      | $0.215 \pm 0.055$                 |

| LP_B2 bulk sample, again from IIC/IID |            |                                   |
|---------------------------------------|------------|-----------------------------------|
| Sample                                | Depth [cm] | $^{240}\text{Pu}/^{239}\text{Pu}$ |
| LP_B2_1                               | 15 - 40    | -                                 |
| LP_B2_2                               | 15 - 40    | -                                 |
| LP_B2_3                               | 15 - 40    | -                                 |

| LP_A bulk sample |            |                                   |
|------------------|------------|-----------------------------------|
| Sample           | Depth [cm] | $^{240}\text{Pu}/^{239}\text{Pu}$ |
| LP_A_1           | 0 - 5      | $0.323 \pm 0.041$                 |
| LP_A_2           | 0 - 5      | $0.222 \pm 0.028$                 |
| LP_A_3           | 0 - 5      | $0.315 \pm 0.057$                 |

**Table 4** Results of  $^{236}\text{U}/^{239}\text{Pu}$  in La Palma soil samples. The measurement uncertainties are given in  $\pm 1\sigma$ .

| Depth profile - IA |                  |                                  |
|--------------------|------------------|----------------------------------|
| Sample             | Core, depth [cm] | $^{236}\text{U}/^{239}\text{Pu}$ |
| LP01a              | IA, 2 - 6        | $14 \pm 3$                       |
| LP02a              | IA, 6 - 8        | -                                |
| LP03               | IA, 8 - 10       | -                                |

| Depth profile - IB |                  |                                  |
|--------------------|------------------|----------------------------------|
| Sample             | Core, depth [cm] | $^{236}\text{U}/^{239}\text{Pu}$ |
| LP04               | IB, 0 - 2        | $3.3 \pm 0.5$                    |
| LP05a              | IB, 2 - 4        | -                                |
| LP06               | IB, 4 - 6        | $0.38 \pm 0.07$                  |
| LP07               | IB, 6 - 8        | $0.27 \pm 0.08$                  |
| LP08a              | IB, 8 - 10       | -                                |
| LP09               | IB, 10 - 12      | -                                |

| Depth profile - IID |                  |                                  |
|---------------------|------------------|----------------------------------|
| Sample              | Core, depth [cm] | $^{236}\text{U}/^{239}\text{Pu}$ |
| LP10                | IID, 0 - 2       | $4.6 \pm 1.5$                    |
| LP11                | IID, 2 - 4       | $0.04 \pm 0.01$                  |
| LP12a               | IID, 4 - 6       | -                                |
| LP13                | IID, 6 - 8       | $0.08 \pm 0.02$                  |
| LP14                | IID, 8 - 10      | -                                |

| IIC bulk sample |                  |                                  |
|-----------------|------------------|----------------------------------|
| Sample          | Core, depth [cm] | $^{236}\text{U}/^{239}\text{Pu}$ |
| LP15a           | IIC, 0 - 8       | $0.14 \pm 0.03$                  |

| LP_B1 bulk sample, again from IIC/IID |            |                                  |
|---------------------------------------|------------|----------------------------------|
| Sample                                | Depth [cm] | $^{236}\text{U}/^{239}\text{Pu}$ |
| LP_B1_1                               | 0 - 5      | $0.23 \pm 0.03$                  |
| LP_B1_2                               | 0 - 5      | $0.17 \pm 0.02$                  |
| LP_B1_3                               | 0 - 5      | $0.21 \pm 0.03$                  |

| LP_B2 bulk sample, again from IIC/IID |            |                                  |
|---------------------------------------|------------|----------------------------------|
| Sample                                | Depth [cm] | $^{236}\text{U}/^{239}\text{Pu}$ |
| LP_B2_1                               | 15 - 40    | -                                |
| LP_B2_2                               | 15 - 40    | -                                |
| LP_B2_3                               | 15 - 40    | -                                |

| LP_A bulk sample |            |                                  |
|------------------|------------|----------------------------------|
| Sample           | Depth [cm] | $^{236}\text{U}/^{239}\text{Pu}$ |
| LP_A_1           | 0 - 5      | $0.78 \pm 0.14$                  |
| LP_A_2           | 0 - 5      | $0.43 \pm 0.08$                  |
| LP_A_3           | 0 - 5      | $0.23 \pm 0.11$                  |

### 3.3.1 Supplementary investigations

Additionally to these soil samples three bulk samples from New Zealand were investigated for their  $^{236}\text{U}/^{238}\text{U}$  and  $^{240}\text{Pu}/^{239}\text{Pu}$  isotopic ratios by AMS. The chemical treatment followed the procedure describe in chapter 6 “Appendix B”. The first sample site was located at S 41° 15.428’, E 175° 01.804’ which is called Barton’s Bush (i.e. forest) and the soil has never been cultivated. The core dimensions were 23 cm deep with 5 cm diameter. The bulk sample was divided in the more organic fraction (labelled ‘NZ\_A’) and the residue (named ‘NZ\_B’). The second sample was collected from the Niue uranium deposit (S 19° 03’ W 169° 55’). If enough material was available, the samples size was between 25 to 30 g for the combustion.

In the following table the obtained values for the  $^{236}\text{U}/^{238}\text{U}$  and  $^{240}\text{Pu}/^{239}\text{Pu}$  ratios are presented. The measurement error is given in  $\pm 1\sigma$ . The sample NZ\_A1 represent the upper surface layer and the  $^{236}\text{U}/^{238}\text{U}$  isotopic ratio was  $(4.67 \pm 0.73) \times 10^{-9}$ . In the layer below the ratio decreased to  $(2.27 \pm 0.28) \times 10^{-9}$ . In Niue the U isotopic ratio was two orders of magnitude lower confirming that the sample was collected from a deposit. All the obtained results of the  $^{240}\text{Pu}/^{239}\text{Pu}$  isotopic ratios show a global fallout signature. According to Kelley et al. [80] the regional average composition of fallout  $^{240}\text{Pu}/^{239}\text{Pu}$  for South Equatorial (latitude, 0-30°S, i.e. Niue) is  $0.173 \pm 0.027$  and for the Southern region (latitude, 30-53°S, i.e. NZ)  $0.185 \pm 0.047$ . The obtained values are in good agreement with the literature.

**Table 12.** The isotopic ratios  $^{236}\text{U}/^{238}\text{U}$  and  $^{240}\text{Pu}/^{239}\text{Pu}$  in soil samples from New Zealand

| Sample | $^{236}\text{U}/^{238}\text{U}$   | $^{240}\text{Pu}/^{239}\text{Pu}$ |
|--------|-----------------------------------|-----------------------------------|
| Niue1  | $(7.68 \pm 0.91) \times 10^{-11}$ | $0.156 \pm 0.041$                 |
| NZ_A1  | $(4.67 \pm 0.73) \times 10^{-9}$  | $0.180 \pm 0.061$                 |
| NZ_B1  | $(2.27 \pm 0.28) \times 10^{-9}$  | $0.165 \pm 0.049$                 |

***Determination of U, Pu and Am isotopes in Irish Sea sediment  
by a combination of AMS and radiometric methods***

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### 3.4 Determination of U, Pu and Am isotopes in Irish Sea sediment by a combination of AMS and radiometric methods

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#### ABSTRACT

Samples from a marine sediment core from the Irish Sea (54.416 N, 3.563 W) were analyzed for the isotopic composition of uranium, plutonium and americium by a combination of radiometric methods and AMS. The radiochemical procedure consisted of a Pu separation step by anion exchange, subsequent U separation by extraction chromatography using UTEVA<sup>®</sup> and finally Am separation with TRU<sup>®</sup> Resin.

Additionally to radiometric determination of these isotopes by alpha spectrometry, the separated samples were also used for the determination of <sup>236</sup>U/<sup>238</sup>U and plutonium isotope ratios by Accelerator Mass Spectrometry (AMS) at the VERA facility.

Keywords: Sellafield, sediment samples, <sup>236</sup>U/<sup>238</sup>U, <sup>240</sup>Pu/<sup>239</sup>Pu, <sup>242</sup>Pu/<sup>239</sup>Pu

#### 1. Introduction

Anthropogenic uranium and transuranium elements like plutonium and americium can be found in the nature because of nuclear weapons testing (e.g. Mururoa, Semipalatinsk), nuclear reactor accidents (Chernobyl), discharges of radioactive waste (Sellafield, La Hague, Mayak) and accidents with nuclear devices, e.g. Palomares and Thule, (Salbu, 2001). This work will

emphasize on sediment samples near the Sellafield reprocessing facility (formerly Windscale) which is located in Cumbria (UK) along the Irish Sea. In the 1950s this facility was used for the production of weapons-grade Pu. Since the 1960s U and Pu are reprocessed from spent fuel in Sellafield (Ketterer and Szechenyi, 2008). Over the past 40 years radionuclides have been discharged from the nuclear fuel reprocessing plant, under the authorization of the government, into the sea and atmosphere (Hu et al., 2010). The magnitude and radionuclide composition of the discharged materials have varied in time depending on factors like the type of the fuel, its burn-up, the nature and duration of storage prior to reprocessing and method of reprocessing (Guéguénat et al., 1996; Cook et al., 1997).

The discharge history of Pu and Am is well documented by Gray et al. (1995) and shows that an estimated total activity of 609 TBq  $^{239}\text{Pu}$ , 22 PBq  $^{241}\text{Pu}$  and 542 TBq  $^{241}\text{Am}$  were discharged to the Irish Sea during the period 1952-92. The peak discharge for these transuranium elements occurred in the mid-to-late 1970s. Afterwards the amount of discharged radionuclides decreased 2 to 3 orders of magnitude due to changes mentioned above. At the beginning the Sellafield operation was focused on the UK weapons program which was associated to low burn-up and therefore a low  $^{240}\text{Pu}/^{239}\text{Pu}$  isotopic ratio. After the late 1960s the major effluent composition was produced from power reactor fuels which had a higher burn-up. According to Kershaw et al. (1995) the isotopic ratio of  $^{240}\text{Pu}/^{239}\text{Pu}$  varied from around 0.05 in the 1960s to 0.25 in 1990s which indicates this effect.

$^{236}\text{U}$  is produced in nuclear reactors mainly by thermal neutron capture on  $^{235}\text{U}$ . A contribution from alpha-decay of  $^{240}\text{Pu}$  is negligible because of its long half-life of 23 Ma and low concentrations in Irish Sea water and sediment (Lee et al., 2008). Due to the reprocessing of spent Magnox fuel rods the BNFL site started at the end of 1950s to discharge tonnes of uranium in an unknown chemical and physical form into the NE Irish Sea. Hamilton and Stevens (1985) have found a  $^{236}\text{U}$  activity of  $10^{-6}$  Bq/g ( $10^9$  atoms/g) in sediment samples from the Esk estuary. In 2001 it could be specified by Hamilton (2001) that since 1969 BNFL has discharged about 80 t of reprocessed depleted uranium, coming from reprocessing waste in uranium cooling ponds and other sources (e.g. Albright & Wilson plant and the BNFL uranium fabrication plant at Springfield). No enhanced uranium concentration in sediments of the NE Irish Sea and estuaries were found; the values are rather typical for sands and silts. Marsden et al. (2001) analysed a sediment core from the Esk Estuary, West Cumbria (UK), located about 5 km south of the marine effluent discharge from BNFL Sellafield for its  $^{236}\text{U}/^{238}\text{U}$  isotopic ratio via Accelerator Mass Spectrometry (AMS). The obtained values were

in the range of  $10^{-5}$  to  $10^{-6}$ , highly above the estimated natural background of  $10^{-14}$  (Zhao et al., 1997).

This work will focus on the determination of  $^{236}\text{U}$ , plutonium and americium isotopes in Irish Sea sediment samples. A sediment core of 48 cm length was collected in 1993 from the Irish Sea at 54.416 latitude and -3.563 longitude during a cruise of the research vessel Gauss, Federal Maritime and Hydrographic Agency, Germany and was divided in two centimeter layers. Samples from the three surface layers down to a depth of 6 cm were taken for analysis and additionally several samples with elevated  $^{241}\text{Am}$  concentrations between 10 cm and 40 cm depth as well as one sample from the 46-48 cm layer (Hrnecek et al., 2002). These samples were chosen for the AMS measurement. Furthermore the procedure was validated by using an IAEA standard (IAEA-368, Pacific Ocean Sediment); the respective U, Pu and Am fractions were measured via alpha spectrometry.

## 2. Materials and methods

### 2.1 Experimental

All reagents were prepared using deionized Milli-Q 18 M $\Omega$ •cm water (Millipore, USA). 65% Suprapure  $\text{HNO}_3$  was purified by sub-boiling distillation. To prevent cross-contamination (with natural U) during the chemical treatment, all laboratory equipment was cleaned with 10%  $\text{HNO}_3$  at least for one day and washed three times with Milli-Q water, subsequently dried in a laminar flow bench and stored in clean zip bags. 30%  $\text{HCl}$ , 30%  $\text{H}_2\text{O}_2$ , 40%  $\text{HF}$  and 25%  $\text{NH}_3$  were of Suprapure grade.

The samples (1 g) were ashed in an electric muffle furnace at 420°C for 24 h. The weighed ashes were dissolved in 20 ml 8M  $\text{HNO}_3$ . Several ash samples were prepared directly for the AMS measurement. The chemical separation of the respective nuclides followed the procedure given by Eichrom Technology Inc. (2005) for U, and for Pu and Am by Hrnecek and Feichtinger (2005) and Moreno et al. (1997). The sample treatment was modified to our needs and is described briefly. The chemical procedure consisted of a Pu separation step from U and Am by anion exchange (Dowex 1x8, 100-200 mesh, Dow Chemical Co.) in 8M  $\text{HNO}_3$  after oxidation state adjustment to Pu(IV). The U was separated from Am by using UTEVA<sup>®</sup> Resin (Eichrom Technologies, LLC) and Am was purified via extraction chromatography using TRU<sup>®</sup> Resin (Eichrom Technologies, LLC). The U chloride and Pu nitrate separated from the sediment samples were measured in the oxide form (details see section 2.3) by AMS

to get information about the isotope ratios  $^{236}\text{U}/^{238}\text{U}$  and  $^{240}\text{Pu}/^{239}\text{Pu}$ , respectively. Furthermore the  $^{241}\text{Am}/^{243}\text{Am}$  ratio was measured in four samples for the comparison between alpha spectrometry and AMS. The yield-monitor-free Pu fractions were controlled for possible  $^{242}\text{Pu}$  interference in the sediment samples.

Selected ash samples given in Table 1 and one reference sample (IAEA-368, Pacific Ocean Sediment) were measured after addition of tracers  $^{243}\text{Am}$  (SRM 4332D),  $^{242}\text{Pu}$  (SRM 4334H) and  $^{232}\text{U}$  (SRM4324B), respectively, in order to check the validity of our results by alpha spectrometry. The radiochemical procedure was the same as described before but for the determination of  $^{238}\text{U}$ ,  $^{238}\text{Pu}$ ,  $^{239(40)}\text{Pu}$  and  $^{241}\text{Am}$  by alpha spectrometry thin sources were prepared by microprecipitation with  $\text{NdF}_3$  (Hindman, 1983).

## 2.2 Alpha spectrometry

Alpha measurements were performed with an OCTÉTETM PC (EG&G Ortec) with ULTRA ion implanted silicon detectors with an active area of  $450\text{ mm}^2$ . For efficiency calibrations an  $^{241}\text{Am}$  source (GT223, AEA Technology) was used. Measurements were evaluated using MAESTRO for Windows software (EG&G Ortec).

## 2.3 Accelerator Mass Spectrometry

After alpha spectrometry, the filters carrying the respective radionuclides were reprocessed for the AMS measurements according to Srncik et al. (2008) with slight modifications. The filters were dissolved in  $\text{HNO}_3/\text{H}_2\text{O}_2$  and evaporated for three times with the same reagents as before. The residue was fumed with conc.  $\text{HCl}$  ( $3\times$ ), taken up in 2 ml conc.  $\text{HCl}$  and transferred to a 50 ml vial. The beaker was washed with 7 ml deionized water and this solution was also added to the vial. Finally 1 ml Fe solution containing 1 mg Fe/ml was added. By adding 25%  $\text{NH}_3$  the actinides were co-precipitated with  $\text{Fe}(\text{OH})_3$  at pH 9. As the Pu fractions separated directly for the AMS measurement were in the nitrate form, the samples were dissolved in conc.  $\text{HCl}$  and fumed three times with the same reagent. The U and Am fraction were already in the chloride form; these were dissolved in 2 ml conc.  $\text{HCl}$  and then the procedure for U, Pu and Am was as described before. After centrifuging, the  $\text{Fe}(\text{OH})_3$  precipitate was dried at  $100^\circ\text{C}$  for 2 h and then combusted at  $800^\circ\text{C}$  in small Quartz tubes. The resulting oxides samples were pressed into aluminium sample holders suitable for the ion source of VERA. The VERA setup as used for actinide measurements is described in Vockenhuber et al. (2003) and Steier et al. (2010). Similar to most AMS facilities, it is based

on sputtering of negative sample ions  $\text{UO}^-$  and  $\text{PuO}^-$ , a first mass separation, and acceleration to 3 MV. Gas stripping to  $\text{U}^{5+}$  and  $\text{Pu}^{5+}$  is used to break up molecular isobars (mainly  $^{235}\text{UOH}^-$  for  $^{236}\text{U}$  and  $^{238}\text{UOH}^-$  for  $^{239}\text{Pu}$ ), and after a second acceleration to 18 MeV and another mass analysis the ion species of interest is identified in a Time-of-Flight (TOF) and energy detector. By these means, AMS achieves the best abundance sensitivity and the lowest detection limits for long-lived actinides (Fifield, 2008). VERA is especially optimized for this application. The ionization yield in the ion source (ca. 1%), the stripping yield to the 5+ charge state (5%) and the TOF detector efficiency (ca. 20%) combine to a total detection efficiency of  $10^{-4}$ , if only one isotope is measured. The measurement of several isotopes on one sample requires switching, which reduces the efficiency on each single species. Due to variations in the total efficiency, only isotopic ratios can be measured precisely. For uranium,  $^{236}\text{U}/^{238}\text{U}$  is used. The  $\text{UO}^-$  current is a rough measure for the uranium concentration in the sputter sample. Under typical ion source conditions, 1  $\mu\text{g}$  of U per mg Fe results typically in 20 pA of ion current, but this number may vary by a factor of three between samples. The samples last for several hours under these conditions. The  $\text{U}^{5+}$  beam current is measured with a Faraday cup, whereas  $^{236}\text{U}^{5+}$  is counted in the TOF detector. To correct for the detector efficiency, the isotopic ratios are calibrated using our in-house standard "Vienna-KkU" (Steier et al., 2008). No such calibration is necessary at the present level of precision, where all isotopes are measured in the TOF detector. Whereas typical environmental samples yield count rates of a few counts per second or less, the concentration of radionuclides in the Irish Sea sediment samples is much higher. Therefore, we reduced the sputter rate in the ion source strongly to maintain acceptable (a few kHz) detector count rates. Only a small part of the samples was consumed under such conditions. The measurement precision was not limited by counting statistics, but by variations of the total efficiency, which is determined from the reproducibility of repeated measurements on the same sample, and by the variation of the ratios measured on different samples of the standard material Vienna-KkU.

### 3. Results and discussion

For the IAEA-368 sample the obtained values are  $(8.5 \pm 0.5) \text{ Bq/kg } ^{238}\text{Pu}$  and  $(33.4 \pm 1.1) \text{ Bq/kg } ^{239(40)}\text{Pu}$ . These values are in good agreement with the recommended value of  $(7.6 - 8.9) \text{ Bq/kg}$  and  $(29.0 - 34.0) \text{ Bq/kg}$  for  $^{238}\text{Pu}$  and  $^{239(40)}\text{Pu}$ , respectively. The activity of  $^{241}\text{Am}$  is  $(1.4 \pm 0.1) \text{ Bq/kg}$  which is also within the confidence interval of  $(1.2 - 1.5) \text{ Bq/kg}$ . The obtained values for  $^{234}\text{U}$  and  $^{238}\text{U}$  are  $(34 \pm 1) \text{ Bq/kg}$  and  $(30 \pm 1) \text{ Bq/kg}$ , respectively. These

are in agreement with the reference values of (21.5 – 44.8) Bq/kg  $^{234}\text{U}$  and (25.0 – 33.0) Bq/kg  $^{238}\text{U}$ . The excellent agreement with this standard indicates the accuracy of our procedure.

The obtained  $^{238}\text{Pu}/^{239(40)}\text{Pu}$  activity ratios from the four selected samples for the alpha spectrometry measurement were compared with a former work published by Perna et al. (2005) (Table 1);  $^{238}\text{Pu}$  was decay corrected to 1<sup>st</sup> December 1993. The samples are in good agreement within the  $1\sigma$  uncertainty.

The depth profile of the  $^{240}\text{Pu}/^{239}\text{Pu}$  isotopic ratios for the samples selected for the AMS measurement along the core is shown in Fig. 1. The obtained values for the Pu isotopic ratio are in the range of 0.20 to 0.33 which indicate a high burn-up of  $^{239}\text{Pu}$ . Due to these results the core depth is too short to show the influence of reprocessing of weapons-grade Pu (low burn-up) from the early 1960s. A contribution from global fallout can be excluded due to the measured  $^{238}\text{Pu}/^{239(40)}\text{Pu}$  activity ratios (Table 1). The value for this origin is  $0.024 \pm 0.004$  (Hardy et al., 1973) and the obtained activity ratios are 0.246 at the surface and 0.187 in the deepest investigated layer which is in agreement with the data from Aston et al. (1985) for Irish Sea intertidal sediments.

A correlation between the radionuclide concentration in the sediment layer and the corresponding quantity of the discharged radionuclide per year is generally difficult to assess as cores are often disturbed by redistribution of the adsorbed actinides e.g. by tidal currents (Kershaw et al., 1990). Also bioturbative mixing of the sediment after deposition complicates the interpretation of e.g. the Pu transport time or the sedimentation rate (Aston et al., 1985). In the Cumbrian near-shore waters of the Irish Sea Pu is usually bound to suspended particulate material and mixed by tidal activity. Pu remains available for re-suspension in this area for more than six years following discharge (McKay and Walker, 1990). In general one can expect an "average integral ratio" on the discharges in the core.

In the four sediment layers from Table 1 also the activity of  $^{242}\text{Pu}$  was determined by investigating analogue samples without adding a tracer (St60: 0-2 cm, 10-12 cm, 22-24 cm, 46-48 cm). By using the activity of the tracer which was determined by alpha spectrometry and the obtained isotopic ratios  $^{242}\text{Pu}/^{239}\text{Pu}$  by AMS from the samples (with and without tracer), the  $^{242}\text{Pu}$  activity for the yield-monitor-free samples could be calculated. In Table 2 the obtained activities of  $^{242}\text{Pu}$  and the  $^{242}\text{Pu}/^{239}\text{Pu}$  isotopic ratios are listed. The typical  $^{242}\text{Pu}/^{239}\text{Pu}$  isotopic composition for Magnox fuel with 5-6 GWd/tU is 0.0159 (Bairiot, 2008). Our results are 60 – 70% lower which indicates a shorter irradiation time.

$^{238}\text{U}$  is relatively soluble and behaves conservatively in seawater. Additional sources of U in this region can come from discharges from the Sellafield plant and a phosphate plant (Marchon) at Whitehaven (Kershaw et al., 1990). Depleted uranium from BNFL was found in sediment samples from the Esk by Hamilton and Stevens (1985). The extent of the depletion depends on the burn-up of the fuel and is assumed to be around 2 000 days. According to Hamilton and Stevens (1985) the Magnox fuel will contain 580 ppm  $^{236}\text{U}/\text{gU}$  which gives an isotopic ratio  $^{236}\text{U}/^{238}\text{U}$  of  $5.84 \times 10^{-4}$ . In Table 3 the isotopic ratios of  $^{236}\text{U}/^{238}\text{U}$  along the core are shown. The values are in the range from  $(1.35 - 4.36) \times 10^{-5}$  and they are clearly above the natural background. An increase of the ratio till 20 cm depth can be noticed which reflects an increase of  $^{236}\text{U}$ . The values are similar to the sediment samples from Esk estuary (Marsden et al., 2001). By comparing the distribution of the  $^{236}\text{U}/^{238}\text{U}$  isotopic ratios it can be noticed that both values show a similar increase down to about 18 cm depth. Afterwards the values decrease rapidly in the Esk estuary samples to a ratio of  $9.2 \times 10^{-6}$ ; here the ratio decreases slightly to about  $3 \times 10^{-5}$ . A possible reason for the difference could be a different sediment composition since the samples are not collected from the same location. According to Kershaw and Young (1988) the additional anthropogenic contribution of  $^{238}\text{U}$  from Sellafield and Marchon is 8 to 15%. Assuming that the isotopic ratio of the Magnox fuel is in the range of  $10^{-4}$  (Hamilton and Stevens, 1985) we see a contribution of about 10% along the core.

The four Irish Sea samples prepared for the alpha spectrometry measurement were spiked with  $^{243}\text{Am}$  and therefore a first comparison with the AMS measurements (Table 4) was possible. The obtained activity ratios of  $^{241}\text{Am}/^{243}\text{Am}$  by alpha spectrometry were transferred to the isotopic ratio. The Am samples were combusted in the muffle furnace at  $800^\circ\text{C}$  in small Quartz tubes (height: 2 cm,  $\varnothing$ : 1 cm) instead of porcelain crucibles (height: 4cm,  $\varnothing$  top: 3 cm,  $\varnothing$  bottom: 2 cm). With the first samples it was noticed that after the combustion the iron oxide was found at the opening and the Quartz lid. As it was impossible to remove the samples from there, the tubes and the lids were washed with hot conc. HCl, the solutions were collected and the iron hydroxide precipitation was repeated. The affected samples were St60 (0-2 cm) and St60 (10-12 cm). In Table 4 the Am results from alpha spectrometry and AMS are presented and they are consistent within  $1\sigma$ , except the St60 (0-2 cm) sample which is consistent within  $2\sigma$ . The mean ratio of AMS/Alpha was  $1.105 \pm 0.014$ . As  $^{241}\text{Am}$  has a relatively short half-life alpha spectrometry is adequate and compared to mass spectrometry techniques the most sensitive method (Vajda and Kim, 2010). We have shown that AMS is in principle applicable

for the determination of Am radionuclides but at the moment due to the high cost of an AMS facility not suitable for routine measurements.

#### **4. Conclusion**

This work was focused on the determination of  $^{236}\text{U}/^{238}\text{U}$  and  $^{240}\text{Pu}/^{239}\text{Pu}$  in layers of an Irish Sea sediment core. The  $^{236}\text{U}/^{238}\text{U}$  isotopic ratios measured by AMS are far above the natural background, showing the applicability of this ratio to trace sources of irradiated U in the environment. The average  $^{240}\text{Pu}/^{239}\text{Pu}$  isotopic ratio is  $0.23 \pm 0.04$  which indicates a high burn-up of  $^{239}\text{Pu}$  and therefore is not weapons-grade Pu. Due to this result the samples show a time scale from the late 1960s till 1990s. The respective U and Pu isotopic ratios show a maximum at the same layer. Additionally, for the first time the isotopic ratio  $^{241}\text{Am}/^{243}\text{Am}$  was measured via AMS and compared with alpha spectrometry measurements. The agreement between the two methods was satisfying.

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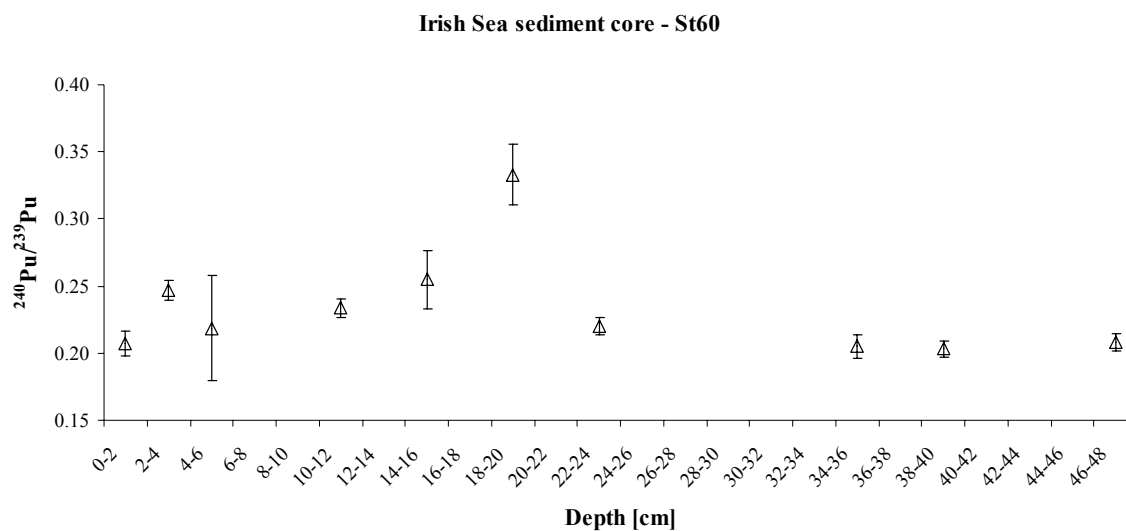
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**Figures captions**

**Fig. 1.** Vertical distribution of  $^{240}\text{Pu}/^{239}\text{Pu}$  ( $\Delta$ ). The measurement uncertainties are given in  $\pm 1\sigma$ .



**Tables and diagrams****Table 1** Comparison of  $^{238}\text{Pu}/^{239(40)}\text{Pu}$  results. The measurement uncertainties are given in  $\pm 1\sigma$ .

| Sample no.     | Perna et al. (2005)                   | This work                             |
|----------------|---------------------------------------|---------------------------------------|
|                | $^{238}\text{Pu}/^{239(40)}\text{Pu}$ | $^{238}\text{Pu}/^{239(40)}\text{Pu}$ |
| St60, 0-2 cm   | $0.246 \pm 0.011$                     | $0.248 \pm 0.006$                     |
| St60, 10-12 cm | $0.241 \pm 0.009$                     | $0.231 \pm 0.007$                     |
| St60, 22-24 cm | $0.215 \pm 0.009$                     | $0.216 \pm 0.007$                     |
| St60, 46-48 cm | $0.187 \pm 0.005$                     | $0.192 \pm 0.006$                     |

**Table 2** Results of the  $^{242}\text{Pu}$  activity [mBq/g] and the isotopic ratio  $^{242}\text{Pu}/^{239}\text{Pu}$  in sediment samples without tracer. The measurement uncertainties are given in  $\pm 1\sigma$ .

| Sample no.     | $^{242}\text{Pu}$ [mBq/g] | $^{242}\text{Pu}/^{239}\text{Pu}$ |
|----------------|---------------------------|-----------------------------------|
| St60, 0-2 cm   | $0.58 \pm 0.05$           | $0.0047 \pm 0.0003$               |
| St60, 10-12 cm | $1.05 \pm 0.12$           | $0.0064 \pm 0.0007$               |
| St60, 22-24 cm | $2.41 \pm 0.13$           | $0.0055 \pm 0.0002$               |
| St60, 46-48 cm | $1.38 \pm 0.18$           | $0.0054 \pm 0.0007$               |

**Table 3**  $^{236}\text{U}/^{238}\text{U}$  results of sediment sample from the Irish Sea. The measurement uncertainties are given in  $\pm 1\sigma$ .

| Sample no.     | $^{236}\text{U}/^{238}\text{U}$  |
|----------------|----------------------------------|
| St60, 0-2 cm   | $(2.41 \pm 0.20) \times 10^{-5}$ |
| St60, 2-4 cm   | $(1.53 \pm 0.11) \times 10^{-5}$ |
| St60, 4-6 cm   | $(1.35 \pm 0.11) \times 10^{-5}$ |
| St60, 10-12 cm | $(2.25 \pm 0.23) \times 10^{-5}$ |
| St60, 14-16 cm | $(4.15 \pm 0.35) \times 10^{-5}$ |
| St60, 18-20 cm | $(4.36 \pm 0.26) \times 10^{-5}$ |
| St60, 22-24 cm | $(3.82 \pm 0.23) \times 10^{-5}$ |
| St60, 34-36 cm | $(3.29 \pm 0.40) \times 10^{-5}$ |
| St60, 38-40 cm | $(3.45 \pm 0.37) \times 10^{-5}$ |
| St60, 46-48 cm | $(2.96 \pm 0.41) \times 10^{-5}$ |

**Table 4** Comparison of the isotopic ratio  $^{241}\text{Am}/^{243}\text{Am}$  by alpha spectrometry and AMS. The measurement uncertainties are given in  $\pm 1\sigma$ .

| sample no.     | alpha spectrometry                | AMS                               |
|----------------|-----------------------------------|-----------------------------------|
|                | $^{241}\text{Am}/^{243}\text{Am}$ | $^{241}\text{Am}/^{243}\text{Am}$ |
| St60, 0-2 cm   | $0.080 \pm 0.002$                 | $0.110 \pm 0.017$                 |
| St60, 10-12 cm | $0.087 \pm 0.002$                 | $0.078 \pm 0.012$                 |
| St60, 22-24 cm | $0.237 \pm 0.006$                 | $0.249 \pm 0.037$                 |
| St60, 46-48 cm | $0.101 \pm 0.003$                 | $0.111 \pm 0.017$                 |



***Uranium extraction from aqueous solutions by ionic liquids***

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### 3.5 Uranium extraction from aqueous solutions by ionic liquids

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#### ABSTRACT

For determining natural levels of  $^{236}\text{U}$  with its environmental abundance of  $10^{-16}$  % rather large sample volumes ( $\sim 30$  L) are necessary, therefore the conventional radiochemical uranium analysis (pre-concentration and column chromatography) is very time consuming. To speed up the procedure hydrophobic ionic liquids (ILs) were evaluated as a potential extraction agent for uranium from aqueous solutions. High selectivity and efficiency for uranium compared to calcium and magnesium in natural water was achieved with tricaprylmethylammonium thiosalicylate, [A336][TS]. Uranium was stripped successfully from the investigated ILs with 2M  $\text{HNO}_3$ .

Keywords: ionic liquids, uranium extraction

#### 1. INTRODUCTION

Naturally occurring uranium consists of three isotopes  $^{234}\text{U}$ ,  $^{235}\text{U}$  and  $^{238}\text{U}$  with an abundance of 0.0055, 0.72 and 99.27 %, respectively. Additionally  $^{236}\text{U}$  ( $T_{1/2} = 23$  Ma) does occur in nature with an isotopic ratio of  $^{236}\text{U}/^{238}\text{U} < 10^{-10}$ . Enhanced levels of  $^{236}\text{U}$  are produced during reactor operation  $^{235}\text{U}(n,\gamma)^{236}\text{U}$  reaction with a cross section of 95 b for thermal neutrons (versus fission cross section of 586 b) (Mironov et al., 2002). Therefore this isotope – or more precisely the atomic ratio  $^{236}\text{U}/^{238}\text{U}$  - is a potential fingerprint for the presence of anthropogenic uranium from nuclear devices in the environment. Accelerator mass spectrometry (AMS) is the only detection technique suitable for  $^{236}\text{U}$  because due to its low natural isotopic abundance it is beyond the capacity of the conventional MS (Chen et al.,

1986), TIMS (Delanghe et al., 2002) and ICP-MS (Becker and Dietze, 2000; Boulyga and Prohaska, 2008) techniques. The sensitivity of  $\sim 10^5$  atoms of  $^{236}\text{U}$  is achievable with AMS (Fifield, 2008). For samples in the ppb range water volumes of 10 – 100 L are required for 10 % counting precision which is associated with a time consuming pre-concentration of uranium: water evaporation followed by column chromatography (Eichrom Technologies, 2001; Krtil et al., 1975). Further, during the evaporation step not only uranium is concentrated but also other matrix elements such as calcium and magnesium, which may display problems during column chromatography (decrease of the drop rate). Looking for an alternative uranium extraction method, we found out that ionic liquids (ILs) were advantageous and so we investigated whether different ILs can be used for (at least) purification or specific extraction of uranium from artificial uranium solutions and later on from a natural water sample.

Ionic liquids, which are organic salts with a melting point below 100 °C and a lack of vapour pressure (Lee, 2006; Wasserscheid and Welton, 2003), have successfully been adopted in recent years e.g. as suitable new solvents for tri-n-butylphosphate (TBP) or dimethylphenylazosalicylfluorone (DMPASF) useable for the extraction of uranium from acidic or seawater matrices (Chang et al., 2008; Binnemans, 2007). Recently, Ouadi et al. (2007) have shown that quaternary ammonium ILs bearing phosphoryl groups exhibit promising properties for the extraction of uranium from acidic water under conditions similar to the PUREX process (Ouadi et al., 2007) and are regarded therefore as task specific for this purpose. These days they are used as solvents in chemical processes (replacing volatile organic compounds) (Lee, 2006), in the nuclear industry for the reprocessing of irradiated nuclear fuel (Bradley et al., 2004), and for the understanding of interactions of biomolecules with uranium species (Gutowski et al., 2007). ILs are also increasingly important for liquid-liquid extraction of metal ions like uranium from NPP (nuclear power plant) waste stream (Küppers, 1998).

In this paper we report on the use of long chain quaternary ammonium ILs with selected aliphatic and aromatic anions (shown in Fig. 1) for their uranium extraction capability from a natural water matrix. To the best of our knowledge no studies for the extraction of uranium from a natural water matrix with pure ionic liquids exist in literature. In liquid-liquid extraction experiments using an uranyl nitrate solution (matrix-free) two ILs with high distribution coefficients were selected for further experiments with uranium in a natural water matrix. Back extraction was performed with different molarities of nitric acid

and satisfying recoveries could be achieved showing the potential of this new method to shorten and simplify the chemical procedure of uranium separation.

## **2. MATERIAL AND METHODS**

### **2.1 Ionic liquids**

Evaluated ILs (shown in Fig. 1) were prepared and characterized according to literature protocols (Kogelnig et al., 2008; Kulkarni et al., 2007; Stojanovic et al., 2008). Briefly, tricaprylmethylammonium methionate, [A336][Met], tricaprylmethylammonium thiocyanate, [A336][SCN], and tricaprylmethylammonium thiosalicylate, [A336][TS], were synthesized applying a deprotonation- or precipitation metathesis route by using tricaprylmethylammonium chloride, Aliquat<sup>®</sup> 336, a cheap industrial product, as cationic precursor.

### **2.2 Instrumental setup**

Uranium activities were measured with a Quantulus 1220 low-level liquid scintillation counter (Wallac Oy, Finland, now Perkin Elmer). By using pulse shape analysis,  $\alpha$ -counts can be clearly distinguished from  $\beta$ -counts.

ICP-MS measurements were conducted using an ELAN 6100 Perkin-Elmer SCIEX spectrometer with a detection limit of 1 ppb for  $^{238}\text{U}$  in the natural water sample. ICP-OES measurements were conducted on an Optima 5300DV Perkin-Elmer spectrometer with a detection limit of 50 ppb for calcium and magnesium, respectively.

### **2.3. Liquid-liquid extraction experiments**

Extraction experiments were conducted by weighting selected amounts of ILs in 15 mL polypropylene tubes, adding 10 mL of deionised water and 10  $\mu\text{L}$  of an uranyl nitrate solution of a known uranium concentration (10  $\mu\text{L}$  is equal to 36  $\mu\text{g}$  U). Samples were shaken over night at 100 rpm and subsequently centrifuged for 30 min at 3500 rpm (the relative centrifugal force (RCF) is 1646) for phase separation. For liquid scintillation counting (LSC) an appropriate amount of the aqueous phase was transferred to a 20 mL LSC vial and was mixed with the scintillation cocktail HiSafeIII<sup>TM</sup>. All samples were measured for 500 min with a pulse shape analysis (PSA) level of 100. The advantage of this measurement system compared to  $\alpha$ -spectrometry is that for our purpose a fast screening is adequate and spectral

resolution of isotopes ( $^{234}\text{U}$  and  $^{238}\text{U}$ ) is not necessary (measuring these samples by  $\alpha$ -spectrometry would require additional sample preparation steps). For ICP-MS or ICP-OES measurements the aqueous phase was properly diluted with 2 % w/w nitric acid.

Distribution coefficients (D) were determined using the following formula:

$$D = \frac{(c_i - c_f)}{c_f} \cdot \frac{m_w}{m_{IL}} \quad (1)$$

Whereas  $c_i$  is the initial concentration in the water phase,  $c_f$  represents the final concentration in the water phase (i.e. after extraction),  $m_w$  indicates the mass of aqueous solution and  $m_{IL}$  is the mass of ionic liquid.

As it is well known that the LSC cocktail HiSafeIII<sup>TM</sup> is miscible with  $\text{HNO}_3$ , we performed the uranium back extraction with 10 mL of 1M, 2M and 7M  $\text{HNO}_3$  solution, respectively. For the back extraction the acids were again shaken over night together with the respective IL. After centrifuging and phase separation an aliquot of the aqueous phase was mixed with the scintillation cocktail and measured by LSC. As the procedure worked well with artificial samples we then investigated a natural water sample from the radon gallery in Badgastein (Salzburg, Austria). This is the well with the highest known  $^{238}\text{U}$  content in Austria ( $\sim 0.1 \mu\text{g/g}$ ) (Steier et al., 2008). The extraction was performed with [A336][SCN] and [A336][TS] and the back extraction with 2M  $\text{HNO}_3$ . These samples were measured by ICP-MS for the uranium determination and by ICP-OES for the calcium and magnesium evaluation.

### 3. RESULTS AND DISCUSSION

Liquid-liquid extraction experiments with the ILs tricaprylmethylammonium methionate, [A336][Met], tricaprylmethylammonium thiocyanate, [A336][SCN], and tricaprylmethylammonium thiosalicylate, [A336][TS], revealed, that uranium was nearly completely extracted with 200 mg of [A336][TS] and [A336][SCN] from 10 mL artificial uranyl nitrate solution containing 36  $\mu\text{g}$  uranium. As it can be seen from Table 1, for [A336][Met] a much higher IL content (1.5 g) was necessary to get at least a significant extraction of  $56 \pm 3 \%$  of U. It is worth mentioning that after the extraction process also with low amounts of [A336][Met] the aqueous phase turned deep red, indicating a remarkable “bleeding” of the IL. Due to this instability we considered [A336][Met] to be unsuitable for further experiments. However, the promising results of [A336][SCN] and [A336][TS] encouraged us to determine their loading capacity. The LSC spectra of the

aqueous phase measured after uranium extraction with 1.5 mg and 42.2 mg [A336][TS] is shown in Fig. 2 (an aliquot of 5 mL was measured). Line [A] represents the reference sample (5 mL water with 18  $\mu\text{g}$  U), line [B] indicates the aqueous phase after extraction (a 5 mL aliquot was measured) and line [C] shows the background (5 mL water). Both ILs exhibited an uptake of approximately 1 mg U/g IL which is equivalent to distribution ratios  $D > 1000$  for uranium between the organic IL and the water phase. Compared to Ouadi et al. (2007), who have evaluated hydrophobic quaternary ammonium ILs for the extraction of U(VI) from aqueous nitric acid solutions with a distribution coefficient of 170 for their phosphoramidate ester-based ionic liquid, our distribution coefficients are significantly higher. However, their task specific IL exhibited a rather high viscosity and had to be diluted in a less viscous and non-functionalized IL. It is known from literature that the extraction efficiency may lead to a decrease in extraction efficiency if task specific ILs for metal extraction processes are diluted in classical solvents or other non-functionalized and cheaper ILs (Visser et al., 2002). In contrary, [A336][TS] and [A336][SCN] evaluated in this work exhibited a suitable low viscosity for their direct application in liquid-liquid extractions without dilution.

Based on our preliminary findings we evaluated the extraction efficiency and selectivity of the ILs [A336][TS] and [A336][SCN] for 10 mL of a natural water matrix with a mean  $^{238}\text{U}$  concentration of 0.1  $\mu\text{g/g}$ . Here [A336][TS] showed a significantly higher efficiency compared to [A336][SCN]. Whereas the  $^{238}\text{U}$  concentration in the aqueous phase after the extraction was below the detection limit of the ICP-MS for [A336][TS] and attaining for this IL a distribution coefficient of  $D > 1000$ , the extraction efficiency for [A336][SCN] was only  $52 \pm 2 \%$ . This is a remarkable difference compared to the results obtained for extraction experiments with the matrix-free solution.

Furthermore, we have determined the affinity of ILs towards the divalent ions calcium and magnesium. Surprisingly, as shown in Table 2, no significant extraction of these two elements could be observed indicating high selectivity of the ILs for uranium compared to magnesium and calcium.

For any further investigation or measurement of uranium it is indispensable to find a suitable method for the back extraction of uranium from the organic IL into an aqueous phase. As it is well known that U(VI) is preferably soluble under acidic conditions,  $\text{HNO}_3$  solutions with different molarities were evaluated as potential stripping agents. 10 mL of a 2M  $\text{HNO}_3$  solution with a back extraction efficiency of  $83 \pm 3 \%$  was found to be most efficient for the

stripping of U from [A336][TS] compared to 1M HNO<sub>3</sub> ( $36 \pm 2$  %) and 7M HNO<sub>3</sub> ( $24 \pm 2$  %).

#### 4. CONCLUSION

Our goal was to find a new method to shorten and simplify the chemical procedure for the determination of uranium in natural water samples, especially for large volumes. The investigated ILs have shown high potential for solving this problem. Hydrophobic ILs containing an aliphatic thiocyanate-, [A336][SCN], or aromatic thiosalicylate anion, [A336][TS], exhibited in both cases a high uranium extraction efficiency from a matrix free water sample. However, extraction experiments from a natural water matrix led to significantly different results: whereas the efficiency for [A336][SCN] was poor, a distribution coefficient of  $D > 1000$  was obtained with [A336][TS] for the elimination of <sup>238</sup>U from natural water with high selectivity compared to the divalent ions magnesium and calcium, which showed no affinity for this IL. Further stripping of uranium from this IL into a 2M HNO<sub>3</sub> solution was also satisfying. In conclusion, [A336][TS] could successfully be applied for pre-concentration of uranium from a natural water matrix. The optimization of this method regarding the extraction mechanism and a possible “up-scaling” for larger water samples is currently investigated in our working group in order to facilitate analytical determinations of the <sup>236</sup>U/<sup>238</sup>U isotopic ratio in natural water samples.

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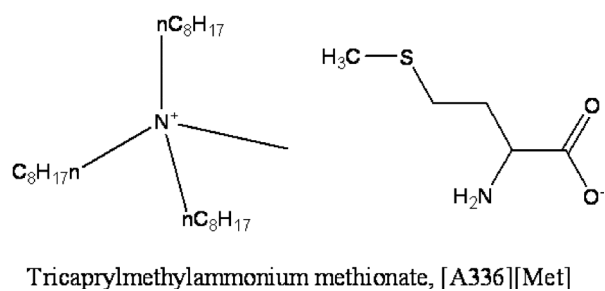
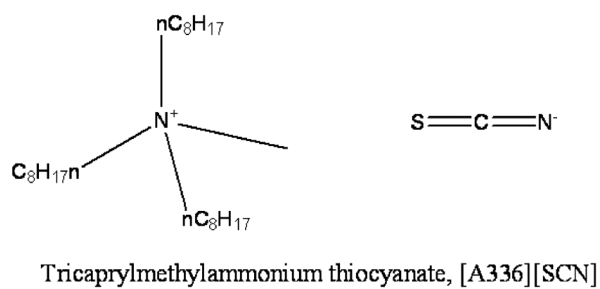
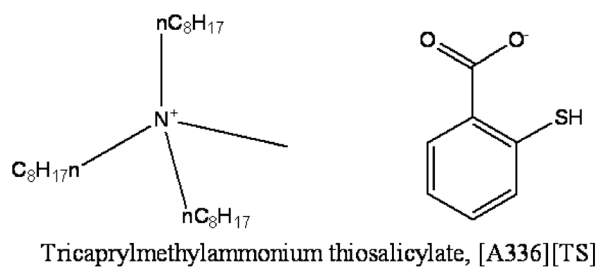
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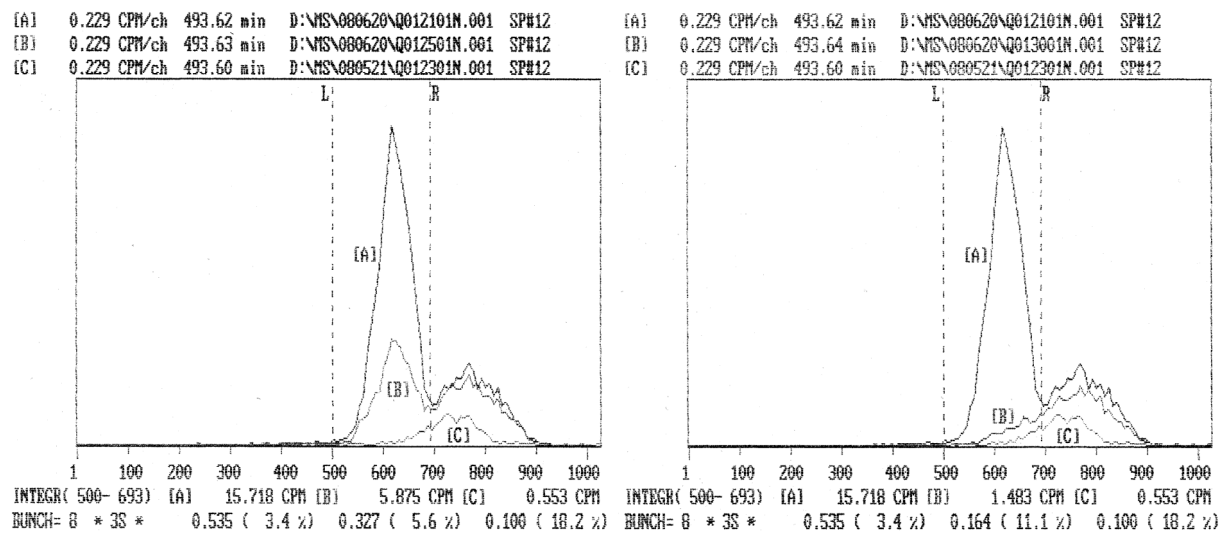
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## Figures captions

**Fig. 1: Chemical structures of evaluated ionic liquids**

**Fig. 2: Uranium extraction with 1.5 mg [A336][TS] (left side) and 42.2 mg (right side). [A] reference sample, [B] sample after uranium extraction, and [C] background.**



**Tables and diagrams****Table 1. Results from the liquid-liquid extraction. The measurement uncertainties are given in  $\pm 1\sigma$ . D indicates the distribution coefficient.**

| IL          | m [g] | U extr. [%] | D        |
|-------------|-------|-------------|----------|
| [A336][Met] | 1.5   | $56 \pm 3$  | -        |
| [A336][SCN] | 0.200 | $98 \pm 1$  | $> 1000$ |
| [A336][TS]  | 0.200 | $98 \pm 1$  | $> 1000$ |

**Table 2: Results for U from the ICP-MS and Ca and Mg from the ICP-OES measurement (b.d.: below detection limit). The uncertainties for ICP-MS and ICP-OES are given in  $\pm 1\sigma$ . D indicates the distribution coefficient for uranium.**

| sample                    | $^{238}\text{U}$ [ $\mu\text{g/L}$ ] | Ca [ $\text{mg/L}$ ] | Mg [ $\text{mg/L}$ ] | D (Uranium) |
|---------------------------|--------------------------------------|----------------------|----------------------|-------------|
| Gasteiner water           | $88 \pm 1$                           | $35 \pm 1$           | $2.03 \pm 0.10$      | -           |
| 50 mg SCN extraction      | $52 \pm 2$                           | $34 \pm 1$           | $2.02 \pm 0.10$      | 141         |
| 52 mg TS extraction       | b.d.                                 | $34 \pm 1$           | $2.01 \pm 0.10$      | > 1000      |
| 50 mg SCN back extraction | $22 \pm 1$                           | -                    | -                    | -           |
| 52 mg TS back extraction  | $71 \pm 1$                           | -                    | -                    | -           |

## 4. Conclusion and Outlook

The aim of these investigations was to develop a method for detecting  $^{236}\text{U}$  in environmental samples by Accelerator Mass Spectrometry (AMS) and to study  $^{236}\text{U}$  in different natural compartments. The described work was structured to start with the analysis of natural samples for the determination of the isotopic ratio  $^{236}\text{U}/^{238}\text{U}$ , followed by water and soil samples from non-contaminated sites and finally anthropogenic sediment samples from the Irish Sea were analysed. The emphasis on this work was the investigation of the  $^{236}\text{U}/^{238}\text{U}$  atomic ratio in environmental samples and for the soil and sediment samples additionally the  $^{240}\text{Pu}/^{239}\text{Pu}$  atom ratio was measured.

Uranium ores and yellow cakes were studied for their  $^{236}\text{U}/^{238}\text{U}$  isotopic ratio by AMS and the potential use of  $^{236}\text{U}$  as a connection link between the feed and product from the same milling facility was explored. As the  $^{236}\text{U}$  production depends on many factors (e.g. neutron flux, water, neutron absorber, etc.) one uranium ore sample from a mine is not representative enough. It indicates more a local isotopic composition. In this work only one of four pairs has shown a good correlation and therefore the yellow cake samples are more useful for the retracing of unknown material at the moment. To establish a suitable database for the usage of  $^{236}\text{U}$  as a nuclear forensic tool much more uranium ores from one mine have to be analysed to get an average isotopic ratio for this location. Additionally, one has to consider that uranium mills often accept ore from different mines which affected the ratio of the yellow cake sample.

Moreover, pre-nuclear materials were investigated for the anthropogenic presence of  $^{236}\text{U}$ . These samples were produced long before any typical anthropogenic contribution, like global fallout or the reactor accident in Chernobyl. Due to this knowledge any enhanced level of  $^{236}\text{U}$  indicates a former irradiation of these materials. The obtained  $^{236}\text{U}/^{238}\text{U}$  isotopic ratios of about  $10^{-10}$  have proven that these samples were not irradiated and due to the rather similar results it can be assumed that the materials are coming from the same uranium ore which was proven by former investigations.

By analysing the respective environmental samples (water and soil samples), which were not influenced by a locally anthropogenic source, it was assumed to find a natural isotopic ratio of  $^{236}\text{U}/^{238}\text{U}$ , especially for the water samples from remote areas in Austria. We expected that waters with springs in the area above the uranium mine in Forstau (Salzburg) might show slightly elevated (natural) levels. But these measurements have shown an anthropogenic

propagation of  $^{236}\text{U}$  in the nature. Also the later analysed water samples have shown an isotopic ratio between  $10^{-7}$  and  $10^{-9}$ . Few parts in  $10^{-9}$  were the lowest obtained values for the investigated samples. The only natural isotopic ratio was measured in the water from the radon galleries in Gastein (Salzburg). An exact identification of the anthropogenic  $^{236}\text{U}$  contribution for the analysed surface water samples is very difficult because of the lack of analysis of a second anthropogenic radionuclide. Due to the obtained results it seems that in Austria an almost omnipresent  $^{236}\text{U}$  contribution from global fallout and/or Chernobyl can be seen.

The investigation of the La Palma soil samples was more successful with regard to the source identification of  $^{236}\text{U}$  due to the measurement of the  $^{240}\text{Pu}/^{239}\text{Pu}$  isotopic ratio. This respective Pu isotopic ratio is a very useful tool to identify the origin of contamination and the obtained results indicated a global fallout signature. The  $^{236}\text{U}$  concentration [atoms/g] was surprisingly high in the surface layer ( $\sim 2$  cm) compared to the following (two orders of magnitude lower). This behaviour was not observed for Pu. The  $^{236}\text{U}/^{238}\text{U}$  isotopic ratios were in the range of  $10^{-7}$  at the surface and  $10^{-9}$  in deeper layers. The calculated  $^{236}\text{U}/^{239}\text{Pu}$  ratios were in the expected range for global fallout.

Additionally sediment samples from the Irish Sea were investigated for their  $^{236}\text{U}/^{238}\text{U}$  and  $^{240}\text{Pu}/^{239}\text{Pu}$  isotopic ratios, respectively. The measured  $^{236}\text{U}/^{238}\text{U}$  ratios by AMS of few parts in  $10^{-5}$  were clearly above the natural background. This study has shown the feasibility to trace sources of irradiated U by means of  $^{236}\text{U}$ . The  $^{240}\text{Pu}/^{239}\text{Pu}$  ratios have shown a high burn-up from  $^{239}\text{Pu}$  for each analysed layer and therefore no weapons-grade Pu was measured. In addition, the  $^{241}\text{Am}/^{243}\text{Am}$  was measured by AMS in four samples for the first time and the results were compared with the respective alpha measurements. It was a satisfactory result and in principle AMS is qualified for the Am isotope measurement but until now it is not suitable for routine measurements compared to alpha spectrometry because of the high costs.

As the conventional radiochemical procedure for the uranium determination (e.g. pre-concentration, column chromatography, etc.) is very time-consuming, a new method to shorten the chemical procedure for water samples was investigated. Extraction experiments of U by ionic liquids (ILs) were carried out. The investigated ILs, an aliphatic thiocyanate- [A336][SCN] and aromatic thiosalicylate anion [A336][TS], have shown a high extraction efficiency for U from an artificial solution. Furthermore experiments with a natural water matrix were conducted. [A336][TS] has displayed a high efficiency and selectivity compared

to divalent ions, like magnesium and calcium. The removal of U from this IL into 2M HNO<sub>3</sub> was satisfying.

This part of the thesis was a first step to show that in principle U can be extracted very easily from a real water matrix. Further experiments have to be done with larger water samples and probably polysulphone “encapsulated” ionic liquids which can be filled in a column; that would simplify the work enormously. This implies no adding of the IL to the water samples, no centrifugation steps, etc., just the passing of the original water sample without pre-treatment through the column, followed by the U elution step.

For the soil samples from La Palma a new chemical procedure with tandem columns was carried out to separate Pu and U from the matrix without any further purification steps. Former procedures consisted of either an additionally Pu or U purification step. The first column was filled with Dowex 1x2 or later Dowex 1x8 because former test have shown that this type of resin was better for the elution of Pu than UTEVA<sup>®</sup>. The second column was filled with UTEVA<sup>®</sup> for the U determination and this column was placed immediately below the first one. This method improved and simplified the chemical treatment for soil samples.

The novelty and importance of this comprehensive study was the measurements of the <sup>236</sup>U/<sup>238</sup>U ratio by AMS in different environmental compartments. This work enables the investigation of the occurrence of both natural and anthropogenic <sup>236</sup>U while up to now <sup>236</sup>U was only measured in uranium ores as well as on anthropogenically affected sites. The detection limits for <sup>236</sup>U/<sup>238</sup>U with conventional mass spectrometry are  $\sim 10^{-10}$  [68] and therefore AMS (especially at the VERA facility) is the only measurement method which is able to reach the detection level required for expected natural concentrations of <sup>236</sup>U/<sup>238</sup>U. This has opened the opportunity to be among the first in the field to investigate the environmental distribution of an ubiquitous, but up to now unexplored isotope.

The investigation of <sup>236</sup>U in the environment could be applied for studies in geology, hydrology, ocean sciences, nuclear safeguards and nuclear forensics. <sup>236</sup>U could be useful as a monitor to investigate the ocean transport by means of effluent uranium or to detect anthropogenic sources in the ocean (e.g. sunken submarines) [13]. Due to the half life of <sup>236</sup>U it could be applied for exposure dating as well as an integrating neutron monitor in geological and environmental studies [81].

## 5. Appendix A: Sample preparation – yellow cake

- Transfer sample in beaker and add 8 ml of 8M HNO<sub>3</sub>.
- Cover each beaker with a watch glass and leach the sample for approximately 1.5 h (soft boiling).
- Cool to room temperature, add 3 – 4 drops of 30% H<sub>2</sub>O<sub>2</sub> and evaporate the solution until near dryness.
- Take up the residue with 5 ml 3M HNO<sub>3</sub>.
- Prepare column with UTEVA<sup>®</sup> resin (1.6 ml), 100 – 150 µm (Eichrom Technologies, Inc.), precondition with 15 ml 3M HNO<sub>3</sub>.
- Load sample onto the column, wash the beaker 2x with 5 ml 3M HNO<sub>3</sub> (waste).
- Elute Th with 30 ml 5M HCl (waste).
- Elute U with 25 ml 1M HCl in 50 ml Greiner tube.
- Evaporate U fraction softly in a heating block.
- Reduce the volume in the tube to around 1 – 2 ml; wash the walls twice with 1 ml 1M HCl.
- Evaporate the samples to dryness.

## 6. Appendix B: Sample preparation – soil samples (New Zealand)

### 1) Leaching

- Put sample (~ 20 g) in 250 ml beaker.
- Ash sample in an electric muffle furnace at 420°C for 24 h.
- Wet sample with some drops of water, add slowly 150 ml 8M HNO<sub>3</sub>, cover beaker with a watch glass and leach samples for 3 h on the hotplate (soft boiling).
- Cool to room temperature, filter solution through a blue ribbon filter paper, wash the beaker 3x with 5 ml 8M HNO<sub>3</sub> (discard filter with insoluble residue).
- Evaporate solution to near dryness.
- Fume 3x with 10 ml conc. HNO<sub>3</sub> and 0.5 ml 30% H<sub>2</sub>O<sub>2</sub>.

### 2) Separation of Pu

- Dissolve residue in 20 ml 1M HNO<sub>3</sub>, add 100 mg Mohr's salt [(NH<sub>4</sub>)<sub>2</sub>Fe(SO<sub>4</sub>)<sub>2</sub>·6H<sub>2</sub>O], add 20 ml conc. HNO<sub>3</sub> and 0.5 g NaNO<sub>2</sub>.
- Prepare column with 6 g Dowex 1x8 (100-200 mesh, Dow Chemical Co) pre-conditioned with 8M HNO<sub>3</sub>.
- Transfer sample to the column, wash beaker 4x with 10 ml 8M HNO<sub>3</sub> and keep these solution (Am, Sr, U fraction).
- Remove Th with 50 ml conc. HCl (waste).
- Elute Pu with 50 ml 0.1M NH<sub>4</sub>I – 9M HCl.
- Evaporate to near dryness and fume 3x with 5 ml conc. HNO<sub>3</sub> and 0.25 ml 30% H<sub>2</sub>O<sub>2</sub>.
- Fume 3x with 5 ml conc. HCl.

### 3) Separation of U

- Evaporate Am, Sr, U fraction to near dryness.
- Fume 3x with 10 ml conc.  $\text{HNO}_3$  and 0.5 ml 30%  $\text{H}_2\text{O}_2$ .
- Take up the residue with 20 ml 3M  $\text{HNO}_3$ .
- Prepare column with UTEVA<sup>®</sup> resin, 100 – 150  $\mu\text{m}$  (Eichrom Technologies, Inc.), precondition with 30 ml 3M  $\text{HNO}_3$ .
- Load sample onto the column, wash the beaker 3x with 10 ml 3M  $\text{HNO}_3$  (Am, Sr).
- Elute Th with 20 ml 5M HCl (waste).
- Elute U with 30 ml 1M HCl in 50 ml Greiner tube.
- Evaporate U fraction softly in a heating block.
- Reduce the volume in the tube to around 1 – 2 ml; wash the wall with 1 ml 1M
- HCl.
- Evaporate the sample to dryness.

### 4) Target preparation

- take up with 2 ml conc. HCl.
- add 7 ml  $\text{H}_2\text{O}$ , 1 ml Fe solution (1 mg Fe/ml).
- add 25%  $\text{NH}_3$  drop by drop.
- reduce pH to 9 by heating in a water bath.
- Centrifuge the precipitate for approximately 10 minutes at 4 000 rpm.
- Decant supernatant and dry precipitate at 100°C for 2h in an electric oven.
- Transfer sample in a small Quartz tube.
- Calcination at 800°C for 2h in a muffle furnace.
- Transfer sample in suitable holder for AMS measurement.

## 7. Curriculum Vitae

### Personal data

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### Education

07 – 12/2009 In-service training at the Institute for Transuranium Elements, Karlsruhe, Germany  
*“Natural background concentrations of U-236 in uranium ores”*  
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06/2009 5<sup>th</sup> Summer School on Actinide Science and Applications, Karlsruhe, Germany

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04/2008 Basic training for radiation protection officer  
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Since 01/2007 Doctoral study at the University of Vienna  
*“Investigation of the <sup>236</sup>U occurrence in the environment”*  
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10/2001 – 12/2006 Study of Chemistry at the University of Vienna  
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09/1993 – 06/2001    Grammar school  
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### **Teaching Experience**

2010/2011              Teaching assistant in *Übung Radiochemie I* (practical course)

2010                    Teaching assistant in *Umweltchemisches Praktikum inklusive Exkursion*  
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### **Skills**

**Languages**            German (native language)  
English (fluently)  
Italian (basic knowledge)  
French (basic knowledge)

**Scientific**            Development of new methods for trace analysis of natural and  
anthropogenic radionuclides in environmental samples (e.g. water, soil  
and sediment samples).  
Experience with Alpha Spectrometry, Gamma Spectrometry, LSC  
(Liquid Scintillation Counting) and AMS (Accelerator Mass  
Spectrometry).

### **Conference contributions (personal attendance only)**

09/2010              Presentation at the 11<sup>th</sup> International Symposium on Environmental  
Radiochemical Analysis, United Kingdom

11/2009              Presentation at the Advanced training course on Illicit Trafficking and  
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09/2009              Presentation at the 13<sup>th</sup> Austrian Chemical Days Conference, Austria

02/2009              Poster at the 22<sup>nd</sup> Seminar Activation Analysis and Gamma-  
spectroscopy (SAAGAS 22), Austria

09/2008              Poster at the 11<sup>th</sup> international conference on accelerator mass  
spectrometry, Italy

- 07/2008                      Poster at the Conference Plutonium Futures “The Science”, France
- 05/2008                      Presentation at the Conference on "Water for Future Generations", China
- 09/2007                      Presentation at the 12<sup>th</sup> Austrian Chemical Days Conference, Austria
- 08/2007                      Poster at the 11<sup>th</sup> International Conference on the “Chemistry and Migration Behaviour of Actinides and Fission Products in the Geosphere”, Migration 2007, Germany

### **Full Papers**

- (1)     M. Srncik, E. Hrnccek, P. Steier, A. Wallner, G. Wallner, P. Bossew  
      “The vertical distribution of  $^{238}\text{Pu}$ ,  $^{239(40)}\text{Pu}$ ,  $^{241}\text{Am}$ ,  $^{90}\text{Sr}$  and  $^{137}\text{Cs}$  in Austrian soil profiles”  
      Radiochim. Acta 96 (2008) 733 – 738.
- (2)     P. Steier, M. Bichler, L. K. Fifield, R. Golser, W. Kutschera, A. Priller, F. Quinto, S. Richter, M. Srncik, P. Terrasi, L. Wacker, A. Wallner, G. Wallner, K. M. Wilcken, E. M. Wild  
      “Natural and anthropogenic  $^{236}\text{U}$  in environmental samples”  
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- (3)     M. Srncik, D. Kogelnig, A. Stojanovic, W. Körner, R. Krachler, G. Wallner  
      “Uranium extraction from aqueous solutions by ionic liquids”  
      Appl. Radiat. Isotopes 67 (2009) 2146 – 2149.
- (4)     F. Quinto, P. Steier, G. Wallner, A. Wallner, M. Srncik, M. Bichler, W. Kutschera, F. Terrasi, A. Petraglia, C. Sabbarese  
      “The first use of  $^{236}\text{U}$  in the general environment and near a shut down Nuclear Power Plant”  
      Appl. Radiat. Isotopes 67 (2009) 1775 – 1780.
- (5)     M. Srncik, P. Steier, G. Wallner  
      “Determination of the isotopic ratio  $^{236}\text{U}/^{238}\text{U}$  in Austrian water samples”  
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- (6)     P. Steier, F. Dellinger, O. Forstner, R. Golser, K. Knie, W. Kutschera, A. Priller, F. Quinto, M. Srncik, F. Terrasi, C. Vockenhuber, A. Wallner, G. Wallner, E. M. Wild  
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- (7) M. Srncik, K. Mayer, E. Hrnccek, M. Wallenius, Z. Varga, P. Steier, G. Wallner  
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