Analysis of ^{236}U and plutonium isotopes, ^{239,240}Pu, on the 1 MV AMS system at the Centro Nacional de Aceleradores, as a potential tool in oceanography

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ABSTRACT

The performance of the 1 MV AMS system at the CNA (Centro Nacional de Aceleradores, Seville, Spain) for ^{236}U and ^{239,240}Pu measurements has been extensively investigated. A very promising ^{236}U/^{238}U abundance sensitivity of about 3×10^{-11} has been recently achieved, and background figures for ^{239}Pu of about 10^6 atoms were reported in the past. These promising results lead to the use of conventional low energy AMS systems for the analysis of ^{236}U and ^{239}Pu and its further application in environmental studies. First ^{236}U results obtained on our AMS system for marine samples (sediments and water) are presented here. Results of two new IAEA reference materials (IAEA-410 and IAEA-412, marine sediments from Pacific Ocean) are reported. The obtained ^{236}U/^{239}Pu atom ratios, of 0.12 and 0.022, respectively, show a dependency with the contamination source (i.e. local fallout from the US tests performed at the Bikini Atoll and general fallout). The results obtained for a third IAEA reference material (IAEA-381, seawater from the Irish Sea), are also presented. In the following, the uranium and plutonium isotopic compositions obtained on a set of 5 intercomparison seawater samples from the Arctic Ocean provided by the ETH Zürich are discussed. By comparing them with the obtained results on the 600 kV AMS facility Tandy at the ETH Zürich, we demonstrate the solidity of the CNA technique for ^{236}U/^{238}U determinations at, at least, 7×10^{-10} level. Finally, these results are discussed in their environmental context.

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1. Introduction

^{236}U ($T_{1/2}$ = 23.4 My) and ^{239}Pu ($T_{1/2}$ = 24,110 y), alpha emitters, are present in the environment due to their natural and anthropogenic production. Their natural way of production is the thermal neutron activation of the two major uranium isotopes, ^{235}U ($T_{1/2}$ = 703.8 My, 0.72% isotopic abundance) and ^{238}U ($T_{1/2}$ = 4468 My, 99.27% isotopic abundance), respectively. The neutron associated to the cosmic radiation and the so-called nucleogenic component (i.e. neutrons produced by the spontaneous fission of ^{238}U or in the (α, n) reactions on light elements) are responsible for these processes. The nucleogenic production is especially enhanced in uranium rich minerals. Indeed, the maximum natural ^{236}U/^{238}U and

^{239}Pu/^{238}U atom ratios have been measured in these samples, ranging from 10^{-12} to 3×10^{-10} and from 2×10^{-13} to 6×10^{-12}, respectively [1]. The minimum ^{236}U/^{238}U atom ratio, of 10^{-14}, is anticipated for deeper layers of rocks. The estimated natural inventory of ^{236}U on Earth is 35 kg [2].

Since the onset of the nuclear energy in the 1940s, the anthropogenic production has overwhelmed those natural inventories. Due to its fissile nature, ^{239}Pu was produced in huge amounts for nuclear weapons and later on for nuclear reactors, in this last case usually combined with the naturally fissile radionuclide ^{235}U. Among the different associated by-products, ^{236}U and ^{240}Pu ($T_{1/2}$ = 6564 y, alpha emitter) deserve special attention. ^{240}Pu is mainly produced by neutron activation of ^{239}Pu; for ^{236}U, the nuclear reaction ^{238}U(n,$3n$) is, in addition to the neutron activation of ^{235}U, an important way of production when fast

neutrons are involved (i.e. thermonuclear atomic weapons). Therefore, the ^{240}Pu/^{239}Pu and the ^{236}U/^{238}U are in close relationship with the nature of the neutron component in a specific nuclear device. Whereas in nuclear detonations they inform about the original design of the gadget and the yield of the detonation; in nuclear reactors, these ratios report about the nature of the fuel (e.g. type of reactor) and the burning times. A comprehensive set of ^{240}Pu/^{239}Pu results has been reported which shows this dependency. For instance, the local fallout at the Trinity Test Site (New Mexico, USA), where the first American nuclear gadgets were tested, is characterized by a ^{240}Pu/^{239}Pu atom ratio of 1.3×10^{-2}, one of the lowest ones reported in the literature [3]. At sites influenced by the Chernobyl accident (1986 in the former Soviet Union, now Ukraine), ^{240}Pu/^{239}Pu atom ratios as high as 0.57 have been reported [4]. However, there is not information about the source dependency of the ^{236}U/^{238}U ratio, due to the dilution effect of the ubiquitous ^{238}U. Therefore, environmental studies of ^{236}U require the use of inventories to identify its source. The baseline level is associated to the ^{236}U that was released worldwide due to the atmospheric nuclear tests, with estimated global inventories ranging from 900 to 1400 kg [5,6]. On the other hand, the Sellafield Nuclear Reprocessing Plant (NRP), in United Kingdom, and La Hague, in Northern France, have released approximately between 115 and 250 kg of ^{236}U to the Northern Seas since 1960, and about 190 kg of ^{239}Pu [7]. The ^{236}U released to the environment represents only about 0.1% of the total budget that is estimated to be stored in nuclear power plants worldwide [6].

In the last years, ^{236}U has been established as a new isotopic tracer in oceanography due to its conservative nature in seawater. It is worth to mention the studies focused on the Pacific Ocean after the Fukushima accident [8] and on the Japan Sea [9], and the ^{236}U studies performed by the ETH Zürich group on the North Atlantic Ocean [6] and the North Sea [10]. Moreover, ^{236}U results in marine sediments have been reported in [9,11]. The development of this new application field has been possible thanks to the low ^{236}U/^{238}U abundance sensitivity provided by Accelerator Mass Spectrometry (AMS), orders of magnitude better than the provided ones by conventional MS techniques. The key is the removal of the uranium molecular isobars (mainly ^{235}U^{1}H) in the so-called stripping process, which occurs in the terminal of a tandem accelerator. With an appropriate ion-optics design of the kinematic filters, the background caused by the neighboring ^{235,238}U molecular fragments can be minimized. Finally, the use of nuclear detectors in a final stage allows the discrimination of the ions of interest. The best ^{236}U/^{238}U background values, of about 10^{-13},

have been achieved on the 14 MV UD AMS facility at the Australian National University (ANU, Canberra, Australia) and on the 3 MV AMS facility at the Vienna Environmental Laboratories (VERA, Vienna, Austria) [1,12]. The 600 kV compact AMS facility at the ETH Zürich features very similar abundance sensitivity, despite the energy gap and its compact design [13]. Recently, it has been demonstrated that an abundance sensitivity of about 3×10^{-11} can be achieved on the 1 MV AMS facility at the Centro Nacional de Aceleradores (CNA, Seville, Spain) [14]. In this context, a potential complementary approach would be the study of the ^{236}U/^{239}Pu ratio. A very reliable range for the global fallout ^{236}U/^{239}Pu ratio of 0.19–0.23 has been obtained from the study of soil cores from different areas of the Northern Hemisphere, far from local actinides sources other than global fallout [5,15,16]. These ratios were deduced using the integrated inventories of ^{239}Pu and ^{236}U along the cores, due to the matrix-dependent profiles of both radionuclides. It is important to note the different physical–chemical behavior of uranium and plutonium, which might be particularly important for non steady state systems, such as seawater masses. Indeed, in surface seawater, the ^{236}U presence is enhanced by at least a factor of 2 over ^{239}Pu, due to the conservative nature of uranium and to the particle-reactive behavior of plutonium, which can be further strengthen in areas with a remarkable biological productivity [17]. For marine sediments, it can be deduced, from published ^{236}U and ^{239,240}Pu data, a few results for reference materials provided by the International Atomic Energy Agency (IAEA) and affected by different local sources. For instance, it can be estimated a ^{236}U/^{239}Pu atom ratio of about 0.09 for sample IAEA-135 [18,19]. This sample was collected at the Irish Sea and is clearly influenced by the discharges from the Sellafield Nuclear Reprocessing Plant (NRP).

In this work, we explore the possibility that offers the 1 MV AMS system at the CNA for ^{236}U and ^{239}Pu studies in Oceanography. For this purpose, two groups of samples have been studied: (i) three reference materials provided by the IAEA: two new marine sediments from the Pacific Ocean (IAEA-410 and IAEA-412) and one seawater sample from the Irish Sea (IAEA-381), and (ii) five seawater samples from the Arctic Ocean provided by the ETH Zürich group. In the case of the seawater samples, our results will be directly compared to the obtained ones by the ETH Zürich group as an intercomparison exercise. The obtained results for the two new IAEA reference materials will add unique information in specific environmental compartments about the rarely studied source-dependent ^{236}U/^{239}Pu atom ratio. The obtained results will be discussed in their corresponding environmental

Table 1
Obtained ^{236}U and ^{239,240}Pu results for the different aliquots of the IAEA-410 and IAEA-412 samples studied on the 1 MV AMS facility at the CNA. The ones leached with HF have been highlighted (*). The ^{236}U/^{238}U atom ratios have been estimated considering the ^{236}U AMS results (leachable fraction) and the ^{238}U data (total fraction) given in the IAEA data evaluation reports [20,21], as explained in the text. The ^{239,240}Pu results have been also included in these IAEA reports.

Sample	Description	^{236}U ($\times 10^6$ atoms/g)	^{236}U/^{238}U ($\times 10^{-9}$ atom ratio)	$^{239+240}$Pu (mBq/g)	^{240}Pu/^{239}Pu (atom ratio)	^{236}U/^{239}Pu (atom ratio)
410–1	IAEA-410 sediment from Bikini Atoll (11°26′N, 164°52′E)	266 ± 17	141 ± 5	6.32 ± 0.14	0.273 ± 0.011	0.112 ± 0.008
410–2		194 ± 22	103 ± 8	4.74 ± 0.11	0.284 ± 0.012	0.111 ± 0.013
410–5		223 ± 14	118 ± 4	5.33 ± 0.12	0.244 ± 0.011	0.105 ± 0.007
410–8*		216 ± 14	114 ± 4	3.76 ± 0.08	0.226 ± 0.009	0.139 ± 0.009
	Average	225 ± 8	120 ± 4	5.04 ± 0.28	0.257 ± 0.005	0.112 ± 0.005
	Std. deviation	26	16	1.07	0.023	0.013
412–2	IAEA-412 sediment from Pacific Ocean (22°23′N, 152°40′E)	6.7 ± 1.9	0.99 ± 0.21	0.578 ± 0.019	0.183 ± 0.012	0.025 ± 0.007
412–3		7.2 ± 1.4	1.06 ± 0.13	0.597 ± 0.018	0.157 ± 0.010	0.025 ± 0.005
412–4*		7.6 ± 0.9	1.12 ± 0.10	0.568 ± 0.017	0.193 ± 0.011	0.030 ± 0.004
412–6*		3.4 ± 0.7	0.50 ± 0.06	0.589 ± 0.015	0.195 ± 0.010	0.013 ± 0.003
412–10*		3.8 ± 1.1	0.56 ± 0.09	0.579 ± 0.018	0.182 ± 0.011	0.014 ± 0.004
	Average	5.7 ± 0.6	0.85 ± 0.11	0.583 ± 0.005	0.182 ± 0.005	0.0218 ± 0.002
	Std. deviation	2	0.29	0.011	0.015	0.008

contexts. Furthermore, the samples characterization, the radio-chemical methods, the measurement technique, and the obtained results will be presented and discussed.

2. Materials and methods

2.1. Samples

The two studied marine sediment samples were provided by the IAEA. The one coded IAEA-410 was sampled at 11°26′N–164°52′E in the Bikini Atoll in 1997, by box coring at 0–24 depth mixture. The sample IAEA-412 was collected at 22°22′N–152°40′E in the Pacific Ocean also in 1997, by box coring at 0–35 m depth. The sediments were first dried in open air and subsequently in heating cabinets at 85 °C. They were then ground into powder, sieved through a 250 um, homogenized and stored in polyethylene flasks [20,21].

In addition, the so-coded IAEA-381 reference seawater sample was also studied. This sample was collected by the IAEA in 1993 during cruising between two shallow stations located at about 54°24′N–3°33′W at 5 m water depth at the Irish Sea, close to the Sellafield liquid discharge area. For this sample, the reported $^{236}U/^{238}U$ atom ratio is at the 10^{-6} level [18,22].

The studied seawater samples were collected during the ARK XVI/3 cruise in the Arctic Ocean (2011). The samples, without a further pretreatment, were directly stored in clean plastic containers and distributed among the laboratories. Two sampling stations were selected for the ETH-CNA intercomparison exercise. Different sampling depths were chosen in each case in order to have a broader range of $^{236}U/^{238}U$ atom ratio (Table 2).

2.2. Radiochemical procedure

Both seawater samples and sediment samples were processed for the sequential separation of the plutonium and the uranium fractions. For sediment samples, 0.5 g aliquots were selected from the sample IAEA-410 and 5 g from the sample IAEA-412. Different masses where chosen according to their origin (i.e. lower actinide concentration was expected in the second case, solely influenced by the general fallout). In the case of the intercomparison seawater samples, 5 l aliquots were used except for the deepest one at station 218, where 10 l were processed. For that sample, very low-levels ^{236}U concentrations were expected.

Samples were spiked with approximately 2 pg of ^{242}Pu and 3 pg of ^{233}U. The sediment samples were then leached with 8 M HNO_3 and H_2O_2 on a hot plate to put in solution the fallout material from the surface of the sediment grains, as discussed in [5]. In some cases, the leaching was enhanced by adding concentrated HF (Table 1). Afterwards, actinides were coprecipitated with $Fe(OH)_3$ after the addition of 50 mg of Fe^{3+} from a standard solution provided by High Purity Standards (HPS, England). For the seawater

samples, the actinides were directly coprecipitated with $Fe(OH)_3$ after the addition of 200 mg of Fe^{3+} from the same standard solution. In both cases, plutonium and uranium were sequentially purified from the iron hydroxides using TEVA® and UTEVA® cartridges, respectively, in tandem in a vacuum box, following the guidelines given in [23,24]. Finally, for the AMS cathode preparation, 1 mg of Fe^{3+} from the HPS standard solution was added to the corresponding uranium and plutonium fractions to coprecipitate them with $Fe(OH)_3$. These precipitates were transferred to quartz crucibles, dried, baked at 600 °C for 1 h to convert the uranium or the pluto-nium to the oxide form, and finally mixed with about 3 mg of Nb powder and pressed into appropriate aluminum cathodes.

In every step, the ^{238}U contamination was minimized using ultra-pure reagents. Glassware was avoided when possible. It is verified that ^{236}U and ^{238}U concentration is negligible in the HPS Fe^{3+} standard solution used in the different $Fe(OH)_3$ preconcentra-tion steps. An instrumental blank was prepared and measured on the Tandy AMS facility at the ETH Zürich, providing negligible fig-ures. The possible $^{239,240}Pu$ and ^{236}U contamination from the ^{242}Pu and ^{233}U spikes was also studied. The ^{242}Pu standard solution sup-plied by National Physical Laboratory (NPL, England) was proved to contain insignificant amounts of any of the radionuclides of inter-est (i.e. $^{239,240}Pu/^{242}Pu$ and $^{236}U/^{242}Pu$ atoms ratios at the 10^{-6} level). However, it was found that the ^{233}U main solution, provided by the IAEA Monaco (unknown supplier) contains ^{236}U at the 10^{-3} level (i.e. $^{236}U/^{233}U$ atom ratio). Therefore, the deepest seawater sample from station 218 was not spiked with ^{233}U, to avoid a potential ^{236}U contamination in the sample. Given that very different environmental samples are routinely processed in our laboratory, a minimum of one chemical blank was included in every batch of samples to control the ^{236}U, $^{239,240}Pu$ and ^{238}U back-ground contributions.

2.3. AMS measurement

Plutonium isotopes, ^{239}Pu and ^{240}Pu, and uranium isotopes, ^{236}U and ^{238}U, were measured on the 1 MV AMS facility at the CNA. Details about the AMS measuring techniques can be found in [14,25]. Shortly, uranium or plutonium isotopes are extracted from the Cs-sputter ion source as oxide anions (i.e. $^{239,240,242}Pu^{16}O^-$ and $^{233,236,238}U^{16}O^-$); analyzed by a 90° sector magnet; injected into the tandem accelerator working at about 670 kV where they are stripped to 3+ (i.e. $^xPu^{3+}$ and $^xU^{3+}$) in Ar gas; and analyzed by a 90° sector magnet and by a 120° electrostatic deflector. The overall transmission through the accelerator is 11%. The less abundant iso-topes (i.e. $^{239,240,242}Pu$ and $^{233,236}U$) are counted from the total energy signal provided by a gas ionization chamber. $^{238}U^{3+}$ is mea-sured as a beam-current in the off-axis Faraday cup (FC3) placed at the exit of the 90° high-energy magnet. The electronics of this FC3 has been recently updated with a new integration range that

Table 2
Uranium and plutonium results for the five intercomparison seawater samples obtained on the 1 MV and on the 600 kV compact AMS systems at the CNA and ETH, respectively. The first number indicates the sampling station; the second one stems for the depth in the water column, in meters. The obtained results for the IAEA-381 reference material are also displayed, and compared with the 95% confidence intervals given in [22] (*). For the sample 204_250, the ^{240}Pu was below the detection limit (LOD), so the $^{240}Pu/^{239}Pu$ atom ratio is not reported. NM stands for "non-measured".

Sample	$^{236}U/^{238}U$ ($\times 10^{-9}$ atom ratio)		^{236}U ($\times 10^6$ atoms/kg)		^{238}U (µg/kg)		$^{240}Pu/^{239}Pu$ (atom ratio)	
	CNA	ETH	CNA	ETH	CNA	ETH	CNA	ETH
IAEA-381	2120 ± 60	2031–2786 (*)	17,300 ± 322	19,726–21,423 (*)	3.22 ± 0.06	3.04–3.84 (*)	0.248 ± 0.007	0.18–0.25 (*)
218_5	2.74 ± 0.16	2.81 ± 0.07	21 ± 1.3	21.9 ± 0.9	3.13 ± 0.08	3.03 ± 0.05	0.35 ± 0.25	0.27 ± 0.06
218_750	2.08 ± 0.09	2.22 ± 0.06	18.6 ± 0.9	20.1 ± 0.8	3.60 ± 0.09	3.55 ± 0.05	0.21 ± 0.04	0.21 ± 0.01
218_1800	0.77 ± 0.05	0.81 ± 0.04	NM	7.1 ± 0.6	NM	3.44 ± 0.08	0.19 ± 0.07	0.20 ± 0.03
204_80	3.1 ± 0.18	2.92 ± 0.09	24.8 ± 1.7	23.9 ± 0.9	3.16 ± 0.12	3.21 ± 0.05	0.15 ± 0.08	0.16 ± 0.02
204_250	2.25 ± 0.11	2.40 ± 0.11	19.7 ± 1.1	19.6 ± 1.1	3.51 ± 0.10	3.21 ± 0.08	(^{240}Pu < LOD)	0.19 ± 0.02

supports the measurement of pA currents, which are the ones usually involved in natural samples [26].

During a routine measurement, the cycling between the different masses is performed using the Slow Sequential Injection System, a pulsing system designed by HVEE that allows the sequential change, in second pulses, of different parameters of the accelerator. In our case, these parameters are the voltage of the low-energy magnet (bouncer) and the terminal voltage. In the case of the rare isotopes, the 120° electrostatic deflector is also adjusted. Every sample is usually measured 13 runs together with standards, instrumental and chemical blanks. In every run, the masses of interest are measured 5 times. The instrumental precision of the measurement is 2%. The total efficiency of the measurement is a factor of 2 higher for plutonium compared to uranium isotopes, probably due to differences in the ionization yields in the Cs-sputtering process. Typical count rates are about 60 cps per pg of every plutonium isotope in a sample, against 30 cps for uranium. This means a total efficiency of about 3×10^{-5} for a normal counting time of 25 min per plutonium isotope (i.e. 2.5% counting statistics error for a sample containing 20 fg, or 0.04 mBq, of ^{239}Pu).

The ^{236}U and ^{239,240}Pu ETH results for the five intercomparison seawater samples were obtained on the 600 kV AMS facility Tandy. Details about the setup and the measurement technique can be found in [13,27] and references therein.

3. Results and discussion

3.1. IAEA reference materials

The uranium results measured for the two new IAEA reference marine sediments, coded 412 and 410, are presented in Table 1. In particular, the ^{236}U atomic concentrations and the ^{236}U/^{238}U and ^{236}U/^{239}Pu atom ratios are shown. The ^{236}U/^{238}U atom ratios were deduced considering the ^{238}U concentrations presented in the IAEA data evaluation reports that were obtained following a total decomposition of the samples [20,21]. This is because the ^{238}U fractions measured by AMS are not representative of the samples, as leaching procedures were applied to extract the fraction of interest (i.e. anthropogenic ^{236}U) as discussed in [5]. The reported ^{239,240}Pu results are also displayed.

It can be concluded from Table 1 that the four analyzed 0.5 g aliquots from IAEA-410 sample show consistent results. The average ^{236}U atom concentration is $(225 \pm 8) \times 10^6$ atoms/kg, and the average ^{236}U/^{238}U atom ratio is $(120 \pm 4) \times 10^{-9}$, where the uncertainties come from error propagation. Each set of results shows a one standard deviation of about 10%, which is a factor of 2 lower than the one associated to the $^{239+240}$Pu activity concentration (with a mean of 5.04 ± 0.28 mBq/g). It is probably that the plutonium present in the sample is more refractory than ^{236}U. Indeed, the non-homogenous Pu results could be due to the leaching techniques, as similar Pu concentrations were reported to the IAEA by those participating laboratories using total decomposition procedures (with a 95% confidence interval ranging from 4.52 to 4.92 mBq/g, [20]). This reference material was taken in the Bikini Atoll where atmospheric nuclear detonations were conducted by United States between 1948 and 1958, with the first megaton test in 1952 [28]. Therefore, it is very likely that it contains plutonium and uranium in refractory forms. The different solubility of the plutonium and ^{236}U fractions will be further studied in a future work.

Much lower uranium and plutonium concentrations have been obtained in the case of the sample IAEA-412 (Table 1). This sample might be solely affected by the general fallout, as it was collected in the Pacific Ocean far from any local source. Therefore, a much more homogenous set of results would have been expected.

Indeed, this is the case of the plutonium results, as the $^{239+240}$Pu activity concentrations and the ^{240}Pu/^{239}Pu atom ratios show standard deviations of 2% and 8%, respectively. However, the ^{236}U results are not that consistent: two out of the five processed aliquots (samples 412–6 and 412–10) provide different results. Specifically, they are about a factor of 2 lower (about 3.5×10^6 atoms/g) than the other three ones (samples IAEA-2, 3 and 4, with about 7×10^6 atoms/g). On average, the ^{236}U concentration is $(5.7 \pm 0.6) \times 10^6$ atoms/g and the ^{236}U/^{238}U atom ratio is $(0.85 \pm 0.11) \times 10^{-9}$. These figures have a standard deviation of about 35% including 412–6 and 412–10. It is interesting to mention that these two samples together with 412–4 were leached with HF. Therefore, it is difficult to explain the lower ^{236}U concentrations obtained. The hypothesis of an error in the added ^{233}U spike is unlikely, given that these samples provide very dissimilar results from the rest, but comparable within each other. This unexpected result, together with the one for sample 410, might be related to the geochemical nature of ^{236}U in the marine environment, which is fairly unknown. Thus, further tests are necessary to find an answer for those data.

In the case of the IAEA-381 reference material (seawater), the CNA ^{238}U concentration is within the IAEA 95% confidence interval (Table 2). However, the ^{236}U concentration approaches that interval from below, 12% apart from the lowest side, and the ^{236}U/^{238}U atom ratio is close to the lowest value that can be estimated considering the reported ^{236}U and ^{238}U information [22]. The most likely explanation for this tendency towards low ^{236}U results is the loss of detection efficiency in the gas ionization chamber due to the high count rates involved in this case, in the kHz range, since dead-time losses are not considered in our routine protocol for low level environmental data evaluation. However, it is important to keep in mind that only information values have been reported for ^{236}U and ^{238}U by the IAEA.

3.2. Intercomparison seawater samples

In Table 2 we present the obtained results for the ETH–CNA intercomparison exercise performed with the five different seawater samples from the Arctic Ocean. The CNA ones are corrected by the instrumental backgrounds (i.e. iron oxide mixed with Nb) that represent the cross contamination in the ion source and, besides, in the case of uranium results, by (i) the ^{236}U contribution of the ^{233}U spike and, (ii) by the ^{236}U background produced by the ^{235}U molecular fragments using the "^{239}Pu"/^{238}U ratio as a proxy, as discussed in [14]. For the ETH results, none of these corrections were necessary. In sample 218_1800 only the uranium isotopic composition is displayed in Table 2 in the case of the CNA, as no ^{233}U spike was added to this sample as explained before.

There is a very good agreement between the ETH and CNA results. This is also true for the sample with the lowest ^{236}U/^{238}U isotopic ratio (218_1800), where the CNA reports $(0.77 \pm 0.05) \times 10^{-9}$ and the ETH $(0.81 \pm 0.04) \times 10^{-9}$. Reaching that isotopic abundance with that accuracy highlights the potential of the CNA facility in this exercise, as the value is a factor of 30 over the abundance sensitivity (i.e. ^{236}U/^{238}U $\sim 3 \times 10^{-11}$ [14]). This means that the applied background corrections are reliable for atomic ratios in this range. This limiting background is at least two orders of magnitude lower in the case of the ETH facility, thanks to the introduction of a second sector magnet on the high-energy side of the spectrometer [13]. The ^{236}U and ^{238}U atomic concentrations in both facilities are also in agreement within errors, which indicate the reliability of the calibration of the ^{233}U CNA spike solution and of the radiochemical procedure used to process the samples.

The biggest discrepancy is found in the precisions of the reported ^{240}Pu/^{239}Pu atom ratios, which in the case of the CNA are at least a factor of 3 above the values obtained at ETH. It is very unlikely

that the problem is the chemical yield, as previous tests performed by alpha-spectrometry indicated similar recoveries for plutonium and uranium, ranging from 70% to 90%. The most likely explanation is the insufficient measuring time dedicated to the plutonium analysis, about 40 min per sample (i.e. 20 min for ^{240}Pu and 15 min for ^{239}Pu). Another reason might be the poor performance of Cs-sputter ion source, which was running at a much lower Cs output during plutonium than during uranium analysis to prevent instabilities. In any case, for similar measurement times and source outputs, a better statistical precision is always expected for the 600 kV AMS system at the ETH. It features a transmission through the accelerator for the 3+ charge state at least a factor of 3 higher than the CNA one, thanks to the use of He as stripper gas [29].

Finally, Table 3 displays the obtained $^{239+240}$Pu activity concentrations for the seawater samples measured at the CNA. For the aliquots processed at the ETH no ^{242}Pu spike was added, so the Pu activity concentrations are not reported. Despite the low efficiency obtained during the plutonium analysis explained above, the uncertainties obtained for the plutonium activity concentrations are low enough to outline a depth profile. A clear $^{239+240}$Pu activity concentration maximum is obtained for the 750 m depth sample due to the well-known remineralization process [30].

3.3. ^{236}U and Pu isotopes as environmental tracers

Discussion of the results in an environmental context shows a contribution of anthropogenic ^{236}U to all the studied samples. The measured ^{236}U/^{238}U atomic ratios are above 10^{-10}, at least 2 orders of magnitude higher than the expected one for natural sources (from 10^{-13} to 10^{-14} [2]). The studied marine sediment samples show ratios consistent with the involved actinides sources in each case. The sample IAEA-410, from Bikini Atoll, shows ^{236}U/^{238}U atom ratios of about 10^{-7}, two orders of magnitude higher than the IAEA-412, due to the influence of the local fallout from the thermonuclear tests conducted at that site. In the case of the intercomparison seawater samples, the most superficial ones show ratios between 2 and 3 times 10^{-9}, approximately in the same range than the ratios associated to general fallout. On the other hand, the ^{236}U/^{238}U ratio measured in the IAEA-381 sample is three orders of magnitude higher than the fallout ratios, as the ^{236}U signal from the Sellafield NRP is obviously clear at the Irish Sea [22].

In Fig. 1, ^{236}U/^{239}Pu average ratios are plotted against the corresponding ^{240}Pu/^{239}Pu ratios for the two studied marine sediments from Pacific Ocean, IAEA-412 and IAEA-410, and other results for the same kind of sample from different areas (Irish Sea [18,19]; North Atlantic Ocean [31]; and Mururoa and Fangataufa atolls [14]). Also, the reported isotopic composition for soils affected by the general fallout from different zones (Australia [32]; Japan [5];

Austria [14]) is displayed. It is observed that both ratios show a clear source dependency.

In the case of marine sediments, the lowest ^{236}U/^{239}Pu atom ratio, of about 3.5×10^{-5}, has been reported for the IAEA-384 sample [14]. As mentioned before, this sample is influenced by the local fallout from the atmospheric tests performed in the French Polynesia (Mururoa and Fangataufa atolls) from 1966 to 1971. This influence can be also noticed in the ^{240}Pu/^{239}Pu atom ratio, of about 0.055, which is within the range of the so-called weapon-grade plutonium (from 0.02 to 0.07). Both ratios reflect the nature of these tests (i.e. low-yield nuclear tests and safety-tests), whose debris usually keep the isotopic composition of the primary fuel [33,34].

Some ^{236}U/^{239}Pu ratios are associated to the general fallout in the Northern Hemisphere and detected using the ^{240}Pu/^{239}Pu range (from 0.16 to 0.19, [35]). Two different results have been considered: (i) IAEA-412 sample from the Pacific Ocean reported in this work (^{236}U/^{239}Pu = 0.0218 ± 0.02) and, (ii) the one obtained for a sediment core collected in the North Atlantic Ocean at the so-called Porcupine Abyssal Plain, with an integrated ^{236}U/^{239}Pu ratio of 0.032 [31]. These ratios are about one order of magnitude lower than the reported ones for soils (Fig. 1). This effect is caused by the solubility of uranium in seawater. In fact, in contrast to its presence in soils, only about 1% of the anthropogenic ^{236}U released to the Oceans is expected to be found in abyssal marine sediments [9], against a 20–35% range for the particle-reactive ^{239}Pu [36].

The IAEA-135 sample must be influenced by the Sellafield NRP since it was collected in the Irish Sea. As discussed before, its ^{239}Pu/^{240}Pu ratio is not dramatically different from global fallout group. However, it differs from the group in the ^{236}U/^{239}Pu isotopic composition, with a ratio of 0.09 [18,19].

Finally, the IAEA-410 sample from the Bikini Atoll shows remarkably higher isotopic ratios (^{236}U/^{239}Pu = 0.112 ± 0.005 and ^{240}Pu/^{239}Pu = 0.257 ± 0.005). These ratios might define the very characteristic uranium and plutonium composition of the local fallout released in the thermonuclear tests (yields up to 15 Mt) that were conducted in the Marshall Islands between 1952 and 1958 by United States [28].

As for the seawater samples, it can be observed in Table 3 that the ^{236}U/^{239}Pu ratios, ranging from 1 to 6, are in agreement with

Table 3
$^{239+240}$Pu activity concentrations and ^{236}U/^{239}Pu atom ratios obtained on the 1 MV AMS system at the CNA for the six studied seawater samples (Table 2). For the sample 218_1800, the ^{236}U results obtained at the ETH have been used for the estimation of the ^{236}U/^{239}Pu atom ratio, as no ^{233}U spike was used for the samples processed at the CNA (see Section 3 in the text) (*). The $^{239+240}$Pu activity concentration for sample 204_250 refers solely to ^{239}Pu, as ^{240}Pu was below the detection limit (**).

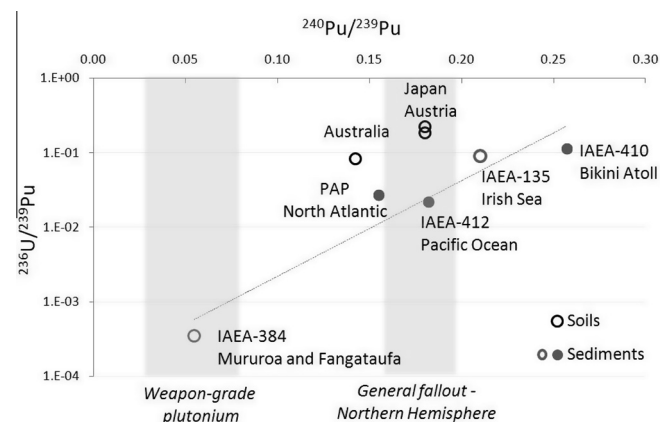| Sample	$^{239+240}$Pu (μBq/kg)	^{236}U/^{239}Pu (atom ratio)
218 _5	8 ± 3	5.8 ± 2.4
218_750	16.4 ± 1.6	1.9 ± 0.2
218_1800	9.40 ± 1.6	1.2 ± 0.2 (*)
204_80	5.70 ± 1.3	6.2 ± 1.3
204_250	1.3 ± 0.8 (**)	14 ± 8
IAEA-381	13.82 ± 0.19 mBq/kg (13.1–14.5 mBq/kg)	2.06 ± 0.04

Fig. 1. Correlation between the ^{240}Pu/^{239}Pu and ^{236}U/^{239}Pu atom ratios for the (i) IAEA-410 and IAEA-412 samples, (ii) a sediment core from the Porcupine Abyssal Plain site (PAP) from the North Atlantic Ocean [31] and, (iii) different soils and marine sediments published elsewhere (empty symbols). The results for the IAEA-384 sample were reported in [14], the ones for IAEA-135 in [18,19], the one for soils from Australia in [32], from Japan in [5], and from Austria (IAEA-Soil-6) in [14]. For the sediment samples, a line has been drawn to guide the eye. The ^{240}Pu/^{239}Pu atom ratios for the weapon-grade plutonium and for the general fallout in the Northern Hemisphere are also indicated.

the measured ones in [17] in samples mostly affected by the general fallout. It is noteworthy that the IAEA-381 sample, with a clear influence of Sellafield discharges, has a $^{236}U/^{239}Pu$ ratio in the same range. The Arctic samples are also influenced by the Sellafield and La Hague NRP [6]. However, the IAEA-135 marine sediment from the Irish Sea (Fig. 1) shows a noticeable different $^{236}U/^{239}Pu$ ratio from the global fallout one, as discussed before. Due to the very different biogeochemical characteristics of both radionuclides in the water, particulate and sediment fractions, this ratio is not expected to be constant in ocean waters in time and space. Besides, $^{236}U/^{239}Pu$ might not be an absolute ratio that can be used to discriminate the origin of the samples. In any case, the data available are scarce, so further sampling and measurements must be undertaken in the future to predict the behavior of ^{236}U in sea water.

4. Summary and conclusions

Our results demonstrate the potential of the 1 MV AMS facility at the CNA for ^{236}U and ^{239}Pu determinations in oceanography studies. The reliability of the CNA ^{236}U measuring technique (sample preparation and AMS determination) has been demonstrated thanks to an intercomparison exercise performed with the ETH Zürich on a set of 5 seawater samples, with $^{236}U/^{238}U$ atom ratios ranging from 7×10^{-10} to 3×10^{-9}. The obtained ^{236}U and ^{239}Pu results on different aliquots of two IAEA reference samples (IAEA-410 and 412) provide new valuable information about the source dependency of the $^{236}U/^{239}Pu$ atom ratio in marine sediments. This information, together with other published results, has been compared with the one provided by the extensively studied $^{240}Pu/^{239}Pu$ atom ratio. Despite the different physical–chemical behavior of both elements, complementary and valuable information can be obtained through the study of both ratios. A much more extensive research is necessary to understand the behavior of anthropogenic ^{236}U in marine samples.

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