

AMS of natural ^{236}U and ^{239}Pu produced in uranium ores

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Available online 3 February 2007

Abstract

The rare isotopes ^{236}U and ^{239}Pu are produced naturally by neutron capture in uranium ores. Here we measure ^{236}U and ^{239}Pu by accelerator mass spectrometry (AMS) in the same ore samples for the first time. To ensure efficient extraction of both elements and isotopic equilibrium between the ^{239}Pu in the ore and a ^{242}Pu spike, we developed a new sample preparation protocol. AMS has clear advantages over previous methods because it achieves better discrimination against molecular interferences with higher sensitivity and shorter counting times. Measurements of ^{236}U and ^{239}Pu hold considerable promise as proxy indicators of neutron flux and uranium concentration.

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PACS: 07.75.+h; 28.41.Rc; 91.65.Dt; 93.85.Np

Keywords: AMS; ^{236}U ; ^{239}Pu ; Uranium ore

1. Introduction

The radionuclides ^{236}U and ^{239}Pu are produced via neutron capture on ^{235}U and ^{238}U , respectively. Both are now widely dispersed in the environment as a result of atmospheric weapons testing and reprocessing operations of spent nuclear fuel. Because of the long half lives of ^{236}U and ^{239}Pu , 2.3×10^7 a and 2.4×10^4 a respectively, these isotopes persist in the environment for periods much longer than human lifetimes. This feature is being turned to advantage by using plutonium as an isotopic tracer for soil erosion and sediment accumulation rates [1]. Plutonium concentrations in sediments and water, together with the $^{240}\text{Pu}/^{239}\text{Pu}$ ratio, have also been used to identify sources of plutonium and to monitor its dispersal away from nuclear facilities [2].

Although the main sources of ^{236}U and ^{239}Pu in present-day environments are anthropogenic, small amounts are

also produced naturally in uranium ores via the same neutron capture reactions as in nuclear weapons and reactors. Naturally occurring ^{239}Pu was first discovered by Seaborg et al. in 1948 in pitchblende from the Great Bear Lakes region of Canada [3]. This discovery was soon confirmed by Peppard et al. who measured ^{239}Pu from Belgian Congo pitchblende [4]. The occurrence of natural ^{239}Pu was subsequently demonstrated in a range of uranium ores as early as 1951 by Levine and Seaborg [5].

Natural $^{236}\text{U}/^{238}\text{U}$ ratios have been measured by several groups [6–10], either by more conventional mass spectroscopic methods or by accelerator mass spectrometry (AMS). However, detection limits with conventional mass spectroscopy for $^{236}\text{U}/^{238}\text{U}$ are $\sim 10^{-10}$, leading to errors larger than 50% for uranium ore samples. Therefore the measurement of natural ^{236}U is difficult or even impossible without AMS [6,8]. AMS offers significant advantages over more conventional mass spectroscopic methods, by making it possible to work with smaller samples, and achieving better discrimination against molecular interferences with higher sensitivity and shorter measurement times. However, even with AMS, measurements of natural $^{236}\text{U}/^{238}\text{U}$

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are challenging because of the interferences from the abundant isotopes ^{235}U and ^{238}U . Consequently, time-of-flight detection and a combination of mass and energy analyzers are required [11].

Applications of natural ^{236}U and ^{239}Pu have been explored by a number of authors. The use of ^{236}U as a neutron flux integrator has been proposed by Purser et al. [12], and was extended a few years later by Valenta [13]. Natural ^{239}Pu has been studied as a natural analogue of the behaviour of plutonium in waste repositories by Fabryka-Martin and Curtis [14]. Furthermore, isotopic “fingerprints” (i.e. characteristic $^{236}\text{U}/^{238}\text{U}$ ratios for particular orebodies) of uranium ores were examined by Richter et al. [8]. In addition to these applications there might be the possibility of using ^{236}U to study the environmental impact of uranium mining by monitoring the levels of ^{236}U in drainage water from the mine. This feature can potentially also be used for uranium exploration by monitoring the levels of ^{236}U in ground water.

In this paper, measurements of both ^{236}U and ^{239}Pu from the same uranium ore samples are reported for the first time. It was necessary to develop a sample preparation protocol that ensured both efficient extraction of plutonium and uranium from the ore and isotopic equilibrium between the ^{239}Pu in the ore and a ^{242}Pu spike. The results obtained in the present work are compared with previous measurements on uranium ores and possible discrepancies are explored.

2. Chemistry and sample preparation

To make precise measurements of the $^{236}\text{U}/^{238}\text{U}$ ratio and ^{239}Pu content in an ore, a sample preparation protocol was developed for the extraction and purification of each element. For efficiency and to ensure that the ^{239}Pu and ^{236}U were products of an identical neutron flux, we separate ^{236}U and ^{239}Pu from the same uranium ore sample. Because of the sensitivity of AMS, a sufficient amount of ^{239}Pu for a measurement can be extracted from less than 1 g of uranium ore. Therefore the following procedure is

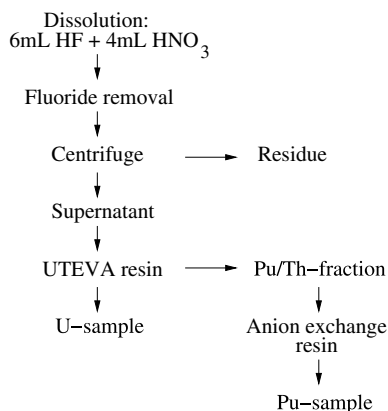


Fig. 1. Schematic diagram of the sample preparation procedure.

designed for only relatively U-rich ($\geq 1\%$ U) samples of less than 1 g. An overview of the protocol is presented schematically in Fig. 1 and is discussed in more detailed in the following sections.

2.1. Dissolution

Initially, the ore material is ground to a fine powder ($<250\ \mu\text{m}$) and thoroughly homogenised. Up to 1 g of sample is weighed into HF-resistant dissolution vials (Teflon). Because ^{239}Pu is the only naturally occurring plutonium isotope, quantitative measurements of its concentration must be made against an artificial tracer. Before dissolution, we added a spike consisting of 4 pg ^{242}Pu in a nitrate solution. In contrast, ^{236}U can be normalised to the abundant isotope ^{238}U .

Whereas efficiency of extraction is not an issue for ^{236}U , because the $^{236}\text{U}/^{238}\text{U}$ ratio is intrinsic to the ore, it is essential that the total inventory of ^{239}Pu is extracted into solution where it can be equilibrated with the ^{242}Pu spike. Consequently, total dissolution of any uranium-bearing minerals is required. Normal leaching methods with HNO_3 or with aqua regia e.g. [1,2,15] are insufficient. Previous approaches [16] have used fusion, in which the sample material is first mixed with an appropriate flux and then fused at high temperature. This approach has the disadvantage that the sample material must typically be mixed with 10–100 times the sample mass of an appropriate flux material, and the actinides must be subsequently separated from this flux. It also fuses unwanted, non-uranium-bearing minerals which contaminate the sample with other elements that must subsequently be separated.

Complete dissolution of uranium-bearing minerals was achieved using dissolution in a mixture of HF and HNO_3 . Nitric acid alone dissolves the bulk of the uranium in ores rich in uraninite, but HF is required to dissolve silicates such as coffinite. This approach has the advantage that it does not dissolve some non-uranium-bearing minerals such as graphite and sulfides common to ores, which can be physically removed. Silica is also effectively separated by volatilisation of silicon tetrafluoride.

Samples were dissolved in a mixture of 6 ml HF and 4 ml HNO_3 at $\sim 70\ ^\circ\text{C}$ under pressure, $\sim 3\ \text{atm}$, for over 24 h. The addition of perchloric acid in early experiments to aid in the expulsion of silicon tetrafluoride was found to reduce yield and was not used in subsequent experiments. After dissolution of silicates and uranium-bearing minerals, an insoluble residue composed mostly of insoluble fluorides, graphite, sulfides and highly resistant oxides typically remained. To recover any plutonium precipitated as a fluoride, fluorine was effectively expelled as HF by two consecutive dry-downs from concentrated nitric acid. Plutonium yields were markedly lower if this step was not included. After fluoride removal, any remaining residue (mostly graphite and sulfides) was centrifuged and the supernatant containing the actinides was collected.

2.2. Isotopic equilibrium

Plutonium commonly exists in four different oxidation states (III, IV, V and VI) in solution. Furthermore, plutonium is reported to exist in all of these states simultaneously [17,18]. It is therefore a possibility that the ^{242}Pu tracer and natural ^{239}Pu are distributed among different oxidation states in the sample solution and are not in valence equilibrium. Consequently, given the different chemical behaviour of plutonium in different valence states, there is the potential that isotopic equilibrium might not be achieved during the extraction chemistry. To investigate this possibility, selected samples were put through a reduction/oxidation cycle in which plutonium was first forced into the 3+ state with a reducing agent (NH_4I) and then oxidized to a higher state with an oxidizing agent (concentrated HNO_3). However, test samples showed that our initial dissolution, which is strongly reducing, is enough to achieve equilibrium between the ^{242}Pu tracer and natural ^{239}Pu , and therefore an additional reduction/oxidation cycle is unnecessary and was subsequently omitted.

2.3. Separation and purification of the actinides

The final phase of the chemistry is separation and purification of plutonium and uranium from the other cations in the solution. This is achieved by using two consecutive ion exchange resins.

First, uranium is separated and purified from the rest of the elements in the rock with uranium tetravalent specific resin (UTEVA, Eichrom Technologies) by loading the sample onto the column in 10 ml 3 M HNO_3 and rinsing with a further 10 ml of 3 M HNO_3 . Under these conditions the resin retains only uranium, plutonium and other tetravalent actinides [19]. The resin is then converted to a chloride system with 5 ml of 9 M HCl . Plutonium and thorium are eluted with 20 ml of 5 M $\text{HCl}/0.05$ M oxalic acid. The oxalic acid strongly reduces sorption of plutonium and thorium while leaving uranium largely unchanged [19]. The eluted Pu-fraction from the UTEVA resin also contains thorium and possibly some uranium, and therefore requires additional separation using an anion exchange resin (Ag 1-X8, Bio-Rad) to purify the plutonium. The plutonium fraction is loaded onto an anion exchange resin in 10 ml of 8 M HNO_3 . Uranium and thorium are then eluted with 25 ml 8 M HNO_3 and 25 ml of 12 M HCl , respectively. Plutonium is then eluted with 25 ml of freshly made, warm (40 °C) 12 M $\text{HCl}-0.1$ M NH_4I . The iodide ion in 12 M HCl reduces plutonium to its trivalent state, breaking the anionic complex and releasing plutonium from the column.

3. AMS methodology

3.1. Measurements of ^{239}Pu

AMS measurements of ^{239}Pu were carried out using the 14 MV accelerator in the Department of Nuclear Physics at

the Australian National University. Plutonium was injected into the accelerator as the PuO^- molecular ion and charge state 5+ was selected after the second accelerator stage following gas stripping in the high-voltage terminal. The accelerator was operated at ~ 4 MV. In broad outline, the methodology is similar to that described by Fifield et al. [21], but performance has been improved significantly by the installation of a new gas stripper system. This gives much better control over the stripper pressure, and has markedly improved the vacuum in the high-energy accelerator tube. The latter in turn, has led to a substantial reduction in the background from ^{238}U ions by about two orders of magnitude, from $\sim 2 \times 10^{-6}$ to $\sim 2 \times 10^{-8}$ of the count rate at the ^{238}U settings. A sample of a certified reference material that contained various plutonium isotopes in accurately known proportions (AEA Technology) was measured to verify that the system was tuned correctly. Reagent blanks had negligible concentrations of ^{239}Pu compared to the uranium ore samples and blank correction was unnecessary.

A major challenge when preparing plutonium samples from uranium ores is to effectively eliminate uranium from the plutonium sample. If this is not achieved, then significant numbers of the $^{238}\text{U}^{17}\text{O}^-$ and $^{238}\text{U}^{16}\text{OH}^-$ molecular ions will be injected into the accelerator simultaneously with the $^{239}\text{Pu}^{16}\text{O}^-$ ion. Consequently, ^{238}U ions can reach the detector because of charge changing collisions in the second accelerator stage and scattering in the beam line. The energy difference between ^{239}Pu and ^{238}U ions is below the resolution of our ionisation chamber, and thus these ions cannot be separated in the detector. However, it is possible to monitor this uranium background by measuring ^{240}Pu . Because natural ores contain negligible amounts of ^{240}Pu , any counts at the ^{240}Pu settings will be due to ^{238}U ions arising from injection of the $^{238}\text{U}^{18}\text{O}^-$ and $^{238}\text{U}^{16}\text{OH}_2^-$ ions. Earlier work [22] showed that the background from these sources was approximately five times greater at the ^{240}Pu settings than at ^{239}Pu , which presumably simply reflects the relative abundances of ^{18}O and ^{17}O . In the course of the present work, a few samples with significant amounts of uranium and negligible amounts of plutonium were also run. The background at ^{240}Pu was found to be 1.5–3 times greater than at ^{239}Pu . The difference between these and the earlier results may represent differences in the relative proportions of the UO^- , UOH^- and UOH_2^- ions. Nevertheless, the background count rate at the ^{240}Pu settings is greater than at the ^{239}Pu settings. For the measurements shown in Table 1, no more than two counts were observed at the ^{240}Pu settings, indicating that uranium background at the ^{239}Pu settings was negligible and that the uranium concentration in the samples was reduced effectively by the sample preparation.

3.2. Measurements of ^{236}U

The ^{236}U measurements were made at VERA (Vienna Environmental Research Accelerator) according to the

Table 1
Measured ^{236}U and ^{239}Pu concentrations in selected ore samples

Sample	U (%)	$^{236}\text{U}/^{238}\text{U}$ (10^{-12})	^{236}U $\frac{10^6 \text{ at}}{\text{g rock}}$	$^{239}\text{Pu}/^{238}\text{U}$ (10^{-14})	^{239}Pu $\frac{10^6 \text{ at}}{\text{g rock}}$
BL-5	7.09 ± 0.03	242 ± 3.5	434 ± 6.2	367 ± 10	6.58 ± 0.18
ANU-0102	14.7 ± 0.2	48.3 ± 1.7	180 ± 6.1	56.5 ± 3.7	1.84 ± 0.12
ANU-099	20.3 ± 0.3	12.3 ± 0.9	62.9 ± 4.5	31.8 ± 2.0	1.70 ± 0.11
ANU-267	42.6 ± 0.5	60.4 ± 1.8	651 ± 19.1	302 ± 13.4	42.91 ± 0.19

Uncertainties (1σ) due to counting statistics alone are shown. An additional 10% uncertainty in the absolute $^{236}\text{U}/^{238}\text{U}$ ratio arises from the uncertainty in the normalisation. (See text for details.)

procedure described earlier in Steier et al. and Vockenhuber et al. [10,11].

The $^{236}\text{U}^{5+}$ ions were identified by a time-of-flight (ToF) system consisting of two microchannel plate assemblies separated by 2.8 m, followed by a Bragg ionisation chamber. Losses occur due to stopping by the grids of the ToF system, due to scattering in the carbon foil of the start detector, and due to small holes in the carbon foils of both start and stop detectors. These foils are mounted on a mesh, and foil is missing from a few of the mesh squares. In addition, because the $^{238}\text{U}^{5+}$ intensity is measured as a current in a Faraday cup between the analyzing magnet and the electrostatic analyzer (ESA), whereas the ^{236}U detection system is after both the ESA and a switching magnet, there are additional transmission losses between the two. In order to determine absolute $^{236}\text{U}/^{238}\text{U}$ ratios, it is necessary to quantify these losses. This was achieved by

- (1) transporting the ^{238}U beam to a Faraday cup between the start and stop detectors, with the start detector withdrawn, to determine the transmission losses, and
- (2) using lower intensity ^{238}U , ^{235}U and ^{234}U ions at counting rates of $\sim 1000 \text{ s}^{-1}$ to determine the efficiency of the detection system. These intensities were achieved by variously attenuating the beam with a passive absorber and by reducing slit apertures, and by using samples that were low in uranium. Several independent measurements of the efficiency were performed.

An efficiency of $31\% \pm 3\%$ was deduced from these measurements. With this efficiency, the in-house standard of Joachimstal uranium ore was found to have a $^{236}\text{U}/^{238}\text{U}$ ratio of $(7.3 \pm 0.7) \times 10^{-11}$, in reasonable agreement with the value of $(6.1 \pm 0.4) \times 10^{-11}$ reported previously [10]. The error (1σ) due to counting statistics for the Joachimstal sample is $\sim 2\%$ and consequently the uncertainty in the measured $^{236}\text{U}/^{238}\text{U}$ ratio is dominated by the uncertainties in the efficiency.

4. Results

The first measurements of natural ^{239}Pu and ^{236}U from the same uranium ores are presented in Table 1. The samples, which cover a range of high-grade uranium ores, were selected because they were expected to contain the highest

concentrations of ^{236}U and ^{239}Pu and would therefore be relatively easy to measure.

The samples ANU-0102 (collected from Boemi (nowadays part of Czech Republic)) and ANU-099 (collected from Val Redena, Italy) are both pitchblende. Sample ANU-267 came from our radioactive material collection and has an unknown origin. Sample BL-5 is a certified reference material for uranium obtained from Natural Resources Canada [20]. Uranium concentrations of the samples were measured with laser ablation inductively-coupled plasma mass spectrometry (ICP-MS) except for the BL-5, which has a known uranium concentration.

It should be emphasized that BL-5 is not a natural uranium ore, but is instead essentially a low-grade concentrate from Beaverlodge, Saskatchewan, Canada, directed at achieving a uranium concentration $\sim 7\%$ [20]. Hence, its average uranium concentration is not representative of its ore component, which is where the ^{236}U and ^{239}Pu would be concentrated. Because of this, the measured ^{236}U and ^{239}Pu concentrations for BL-5 cannot be directly compared with the other samples. This sample was included because its plutonium content had been measured previously [16].

5. Discussion and conclusions

The production of ^{236}U and ^{239}Pu in uranium ores via neutron capture on ^{235}U and ^{238}U , respectively, is determined by both the neutron flux in the ore, and the probabilities of neutron capture by uranium isotopes. The factors that influence these processes are as follows:

- (1) The dominant contributions to neutron production in the ore are the spontaneous fission of ^{238}U , and (α, n) -reactions on light elements such as Li, Be, B, Na, Mg and Al. Rocks with high concentrations of these elements will produce significantly more neutrons than, e.g. quartz which has a relatively low (α, n) neutron yield.
- (2) ^{236}U is produced largely via capture of thermal neutrons. In contrast, ^{239}Pu is produced essentially only via neutron capture in the resonance region. Consequently, the relative and absolute abundances of ^{236}U and ^{239}Pu depend sensitively on the thermalisation process (particularly the presence of water) and on the concentrations of trace neutron absorbers such as Gd and Sm.

Clearly, a proper treatment of this problem requires both a detailed model that incorporates neutron production, thermalisation and capture, and an extensive chemical analysis of the rock matrix that includes the major elements as well as trace neutron absorbers. In particular, any attempt to model production of ^{239}Pu and ^{236}U in uranium ores must take into account the strong absorption of epithermal neutrons by uranium. For this reason, the simple neutron transport model presented by Fabryka-Martin [24] is not appropriate for high uranium concentrations because it is based on the assumption that the neutron flux is not materially reduced by neutron absorption in the epithermal region. Therefore we are currently in the process of modifying the model for high-grade uranium ores to realistically investigate the dependence of the ^{239}Pu concentration and the $^{236}\text{U}/^{238}\text{U}$ ratio on uranium concentration and rock composition.

The most comprehensive set of measurements of $^{236}\text{U}/^{238}\text{U}$ ratios for a range of uranium ores are those of Berkovits et al. [9]. These values range from 12×10^{-12} to 330×10^{-12} for uranium concentrations from 20% to 79%. The values reported here also fall within this range as can be seen from Fig. 2(a). However there is no clear correlation between the uranium concentration and the $^{236}\text{U}/^{238}\text{U}$ ratio. The measurements for BL-5 are not included in Fig. 2 because, as noted above, it is not representative ore material. Indeed, the measured $^{236}\text{U}/^{238}\text{U}$ ratio for BL-5 is higher than the sample with the highest U concentration measured in the present work (ANU-267), and is comparable with the ratios measured in the Cigar Lake deposits by Berkovits et al. and Zhao et al. [9,7].

For natural ^{239}Pu , our measurements are in general lower than earlier measurements on samples with similar uranium concentrations. Early measurements by Levine et al. using α -particle spectroscopy are in the range of 1×10^8 to 120×10^8 atoms of ^{239}Pu per gram of rock for uranium concentrations between 10% and 50% [5]. More recent data obtained with thermal ionisation mass spectrometry (TIMS) by Curtis et al. for uranium concentrations from 3.8% to 55% span a similar range from 3×10^8 to 140×10^8 atoms of ^{239}Pu per gram of rock [23]. Different rock matrixes can, however, have a dramatic effect on plutonium production, and provide a possible explanation for the generally lower values measured in the present work. For example, two of the samples measured by Levine et al. with similar uranium concentrations of 13.5% and 10%, have ^{239}Pu concentrations that differ by a factor of 20 [5]. Similarly, Curtis et al. report a factor of 8 difference in ^{239}Pu concentrations for samples with uranium concentrations of 3.8% and 4.1%. This sensitivity to the rock composition arises because plutonium production is due principally to capture of epithermal neutrons, i.e. with energies in the resonance region. Uranium is a strong neutron absorber in the resonance region, and hence plutonium production will be very sensitive to how rapidly the neutrons pass through the epithermal region. In particular, any water circulating through the ore body will dramatically decrease plutonium production.

Because the production of ^{236}U and ^{239}Pu is dependent on the rock matrix and its environment, it is difficult to compare the present data with earlier results. Only for BL-5, which is readily available as a reference material, is a direct comparison possible. Its ^{239}Pu content has been

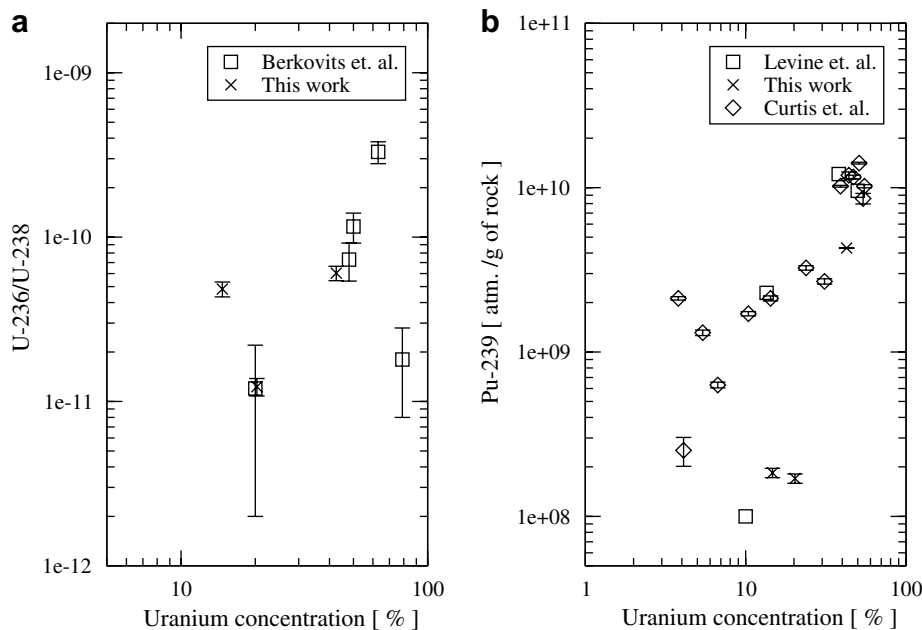


Fig. 2. Measured concentrations of ^{236}U and ^{239}Pu as a function of uranium in the ore compared with earlier measurements [9,5,23]. No uncertainties are available for the data from Levine et al.

measured previously by Dixon et al. [16] using TIMS. Even here there is ambiguity, however, because they present two values, $(6.0 \pm 0.8) \times 10^8$ or $(25.4 \pm 0.4) \times 10^8$ atoms of ^{239}Pu per gram of rock. Of these values, Dixon et al. prefer the higher value because the difference is argued to be due to incomplete dissolution of the sample which yielded the lower value. Our value, on the other hand, agrees within errors with the lower value. Because our AMS measurement is free from molecular interferences, whereas with TIMS it is difficult to separate possible molecular isobars from the ion of interest, and because our dissolution method dissolved all of the uranium-bearing minerals and left only a small low-uranium residue, we believe that the lower value is correct.

To conclude, an AMS methodology for natural ^{236}U and ^{239}Pu has been presented. AMS is preferred over more conventional mass spectroscopic tools because it is possible to work with smaller samples, and achieves better discrimination against molecular interferences with higher sensitivity and shorter measurement times. Consequently, this methodology improves the possibility of investigating the levels of natural ^{236}U and ^{239}Pu in subsurface environments.

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