

Attempt to detect primordial ^{244}Pu on Earth

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With a half-life of 81.1 Myr, ^{244}Pu could be both the heaviest and the shortest-lived nuclide present on Earth as a relic of the last supernova(e) that occurred before the formation of the Solar System. Hoffman *et al.* [[Nature \(London\) 234, 132 \(1971\)](#)] reported on the detection of this nuclide (1.0×10^{-18} g $^{244}\text{Pu}/\text{g}$) in the rare-earth mineral bastnäsite with the use of a mass spectrometer. Up to now these findings were never reassessed. We describe the search for primordial ^{244}Pu in a sample of bastnäsite with the method of accelerator mass spectrometry (AMS). It was performed with a highly sensitive setup, identifying the ions by the determination of their time-of-flight and energy. Using AMS, the stripping to high charge states allows the suppression of any molecular interference. During our measurements we observed no event of ^{244}Pu . Therefore, we can give an upper limit for the abundance of ^{244}Pu in our sample of the mineral bastnäsite of 370 atoms per gram (1.5×10^{-19} g $^{244}\text{Pu}/\text{g}$). The concentration of ^{244}Pu in our sample of bastnäsite is significantly lower than the previously determined value.

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I. INTRODUCTION

Plutonium of natural origin can exist on Earth in its isotopes 239 and 244. ^{239}Pu ($t_{1/2} = 24.1$ kyr) is continuously created in uranium ores and was first observed by Seaborg and Perlman [1]. Primordial ^{244}Pu with $t_{1/2} = 81.1 \pm 0.3$ Myr (α decay, $t_{1/2} = 81.2 \pm 0.3$ Myr [2]; spontaneous fission, $t_{1/2} = 66 \pm 2$ Gyr [3]) was reported in the mineral bastnäsite by Hoffman *et al.* [4]. This long-lived plutonium isotope is supposed to be a relic from one or more core collapse supernova explosions shortly before the formation of Earth, when it was produced during the *r*-process [5]. ^{244}Pu from the ongoing nucleosynthesis in our galaxy [6] is deposited by the flux of interstellar matter onto Earth. Several studies have searched for ^{244}Pu from interstellar dust input in sediments [7–9] and some have possibly found it in manganese crusts [10,11].

The observation of primordial plutonium in bastnäsite [(Ce,La)CO₃F], a fluorocarbonate rare-earth mineral, has up to now never been confirmed. ^{244}Pu was measured in the mineral

bastnäsite by an indirect method determining the excess of fission tracks [12] produced by the decay of ^{244}Pu in the early phase of Earth's history. This study could neither verify nor disprove the existence of ^{244}Pu because of the later thermal extinction of these tracks. Only a previous experiment [13] had also detected ^{244}Pu in a natural sample, the mineral gadolinite [(Ce,La,Nd,Y)₃FeBe₂Si₂O₁₀]. However, in this case the abundance of ^{244}Pu and other plutonium isotopes was so high that it had to be attributed to a contamination. The isotopic signature of plutonium can be used to distinguish an astrophysical from an anthropogenic origin. Plutonium produced in astrophysical processes has to be transported over long distances before it reaches the Solar System. From this origin only the longest-lived isotope ^{244}Pu may be expected to be present on Earth. In contrast, anthropogenic plutonium consists mostly of the lighter isotopes with mass numbers 238–242.

A possible input of ^{244}Pu in bastnäsite from cosmic radiation as discussed by Hoffman *et al.* [4] is not taken into account in this article: Direct determinations of the elemental composition of the cosmic radiation with the use of combined plastic detectors and nuclear emulsions [14] had led to the assumption that natural ^{244}Pu is deposited continuously on Earth. Hence, ^{244}Pu should be distributed rather homogeneously on Earth's surface. But these findings were not confirmed by later experiments [15,16]. According to the result of Hoffman *et al.* [4], ^{244}Pu therefore is the heaviest primordial element on Earth. In the following, we focus on the primordial origin of ^{244}Pu , which is believed to be enriched in the mineral bastnäsite because of the homologous behavior of plutonium and the rare-earth elements.

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II. SAMPLE CHARACTERIZATION AND CHEMICAL PREPARATION

A. Sample characterization

The main differences concerning the sample processing of Hoffman *et al.* [4] and of this work originate from the different initial states in which the material was received. Therefore, the samples used in both studies are compared briefly.

From the same mine as Hoffman *et al.* [4], the Mountain Pass Mine in California, we received two batches (I and II in Table I, Lot No. 4100-06-1120-1) of the product ‘bastnäsite leached and calcined.’ The company Molycorp, Inc., operated the Mountain Pass Mine and enriched the bastnäsite used in this study. At the time the material was purchased, the mining and processing were not active any more, and the only material available from the Mountain Pass Mine was from stock and sold by Molycorp, Inc., and Chevron. This material consisted mainly of CeO₂ (~44%), La₂O₃ (~29%), and Nd₂O₃ (~10%). This fine-grained sand underwent several steps of rare-earth enrichment from the raw ore: A flotation process concentrated the bastnäsite ore from a concentration of ca. 10% rare-earth oxides (REO) to ca. 60% total REO. This material was then leached in a weak acid process to improve the grade to ca. 70% total REO by removing calcium and strontium carbonate impurities. The product of this step was calcined to convert carbonates to oxides, leading to the formation of a rare-earth oxyfluoride. In this paper, this purified material is referred to as bastnäsite. The uranium and thorium contents of the ore were determined by means of α spectrometry to be $(8.72 \pm 0.14) \times 10^{-5}$ g ²³⁸U per g bastnäsite and $(1.42 \pm 0.03) \times 10^{-3}$ g ²³²Th per g bastnäsite, respectively.

The sample of Hoffman *et al.* [4] was initially available in organic HDEHP [bis(2-ethylhexyl)phosphate] and corresponded to 8.5 kg of bastnäsite mineral. During the industrial chemical procedure of separating the rare earths from the bulk mineral, the HDEHP is a later stage than the leached and calcined bastnäsite.

The concentration of rare earths in the bastnäsite mineral of Hoffman *et al.* [4] (~40% CeO₂) is similar to the concentration in the bastnäsite we obtained and described above. Therefore, to compare the concentrations of ²⁴⁴Pu, which are given relative to the amount of sample material, we equate the bastnäsite mineral of Hoffman *et al.* [4] with the leached and calcined bastnäsite used in our study.

In the experiment of Hoffman *et al.* [4], the leached and calcined bastnäsite had been further roasted to convert Ce(III) to Ce(IV). Trivalent rare earths were separated by weak acid leaching. After the dissolution of the CeO₂ the liquid-liquid extractant HDEHP was used to extract the IV-valent cerium and plutonium from the acid.

B. Production of the ²³⁶Pu tracer

²³⁶Pu was produced to trace the yields of the chemical separation and of the accelerator mass spectrometry (AMS) measurements. At the MLL tandem accelerator in Garching a ²³⁸U target was irradiated with protons inducing a ($p,3n\beta^-$) reaction. The approach was similar to the procedure described by Aaltonen *et al.* [17,18]. Natural and previously not irradiated uranium was used as the target for the reaction.

After the irradiation the target was dissolved. The solution containing uranium, ²³⁶Pu, and fission products was purified on anion-exchange columns. During the irradiation, not only ²³⁶Pu but also ²³⁶U and ²³⁶Np in its long-lived ground state were produced. These two nuclides of mass 236 could not have been fully distinguished from ²³⁶Pu during the final AMS measurement and hence would have pretended a too high AMS efficiency for plutonium. Also a large content of ²³⁵U in the sample would have caused problems during the AMS measurement. A high counting rate of ²³⁵U can lead to interference with the time-of-flight (TOF) signal of ²³⁶Pu. To avoid this, uranium and neptunium were separated from plutonium on the strongly basic anion-exchange resin Amberlite IRA 402-Cl several times: This was first done during the tracer purification and later during the sample purification in a process explained below and related to the one described by Michel *et al.* [19].

The advantage of producing ²³⁶Pu via the irradiation of ²³⁸U was that thereby no ²⁴⁴Pu could be created in the carrier.

C. Chemical separation

In our work, the first step of the chemical processing in the laboratory was the dissolution of portions of 150 g mineral in 1 l aqua regia (3:1 volume mixture of HCl and HNO₃) at a temperature of 80 °C for several days. This was carried on until only silicates remained. An amount of about 10% of the original mass was left over. Because of its expected geochemical enrichment similar to the rare-earth elements, plutonium was expected to be dissolved along with these elements and not to remain in the solid silicate fraction.

At the start of the dissolution 80 Bq of the tracer ²³⁶Pu was added to the solution in HNO₃ and was mixed by stirring and heating. The ²³⁶Pu was used in the following to monitor the efficiencies of the chemical processing and of the AMS measurement.

By adding the tracer already when dissolving the sample, it was possible to trace plutonium quantitatively from a starting point earlier than that of Hoffman *et al.* [4].

The dissolution of the bastnäsite is a critical point in the chemical separation. Any ²⁴⁴Pu incorporated in the silicate fraction is lost for the further separation. In addition, any plutonium being attached to the silicate residues in the dissolution process will also be lost. The ²³⁶Pu tracer was added immediately at the beginning of the dissolution. The isotopes ²⁴⁴Pu and ²³⁶Pu could equilibrate in the aqua regia/bastnäsite dissolution for 2 days at minimum. Both isotopes should be affected in the same way by any processes transferring plutonium from the dissolved phase to the silicate residue. Losses of ²⁴⁴Pu in such a process therefore were monitored by the tracer ²³⁶Pu.

The solution of aqua regia, in which all plutonium should be present in the IV-valent state because of the strong oxidizing effect of aqua regia, was diluted to about 8 M acidic solution. To guarantee a similar starting point as Hoffman *et al.* [4], a liquid-liquid extraction with 200 ml 0.7 M HDEHP in *n*-heptane followed [20,21], where the plutonium was transferred into the organic HDEHP phase.

Thereafter, the chemical separation procedure of plutonium was analog to the one described by Hoffman *et al.* [4]: Several

TABLE I. Characteristics of the individual samples measured in the search for ^{244}Pu .

Sample	Mass	Liq.-liq. extr. efficiency	Total chemical efficiency	AMS efficiency	236 run time	244 run time	One count equiv. concentration	Upper limit (99% C.L.)
IG	150 g	91%	39%	2.7×10^{-5}	4.1 h	36.2 h	630 atoms/g	3700 atoms/g
IH	150 g	98%	81%	4.6×10^{-5}	4.1 h	69.1 h	180 atoms/g	1100 atoms/g
IJ	150 g	84%	54%	9.7×10^{-5}	3.0 h	48.6 h	130 atoms/g	750 atoms/g
IIA	150 g	90%	42%	0.9×10^{-5}	1.3 h	12.4 h	1800 atoms/g	11000 atoms/g
IIB	150 g	90%	27%	2.2×10^{-5}	3.0 h	14.6 h	1100 atoms/g	6600 atom/g

washing steps with HCl removed remnants of cerium from the HDEHP solution until no more discoloring was visible in the washing portions. Back extraction of the plutonium required the reduction of Pu(IV) to Pu(III). The reduction was conducted by the addition of the organic extractant DBHQ (di-tert-butylhydroquinone) in 2-EHOH (2-ethylhexanol) to the HDEHP in a volume ratio of 1/3 to assure full reduction of the plutonium [22]. In five portions, each with 50 ml 6 M HCl, the plutonium was extracted from the organic solvent. By adding NaNO_2 to the 250 ml 6 M HCl the plutonium was oxidized back to the IV-valent state. Usually, 90% of the initially added tracer could be recovered after this purification with HDEHP (Table I).

The HCl solution containing the plutonium was purified on a strongly basic anion-exchange column of the type Amberlite IRA 402 Cl^- following Michel *et al.* [19]. It was eluted from the column with 0.1 M NH_4I in 6 M HCl. This solution was evaporated to dryness, the iodine was removed by adding HNO_3 several times. The last purification process on the column was repeated until only some milligrams of material remained.

The yield for plutonium in the chemical purification varied from 27% to 81% (Table I).

For better sputtering properties in the ion source, the purified material was mixed with 5 mg of iron powder. This sample was then again dissolved in HNO_3 for homogenization and dried on a hot plate. Finally, the material was oxidized for several hours at a temperature of 500 °C.

III. MEASUREMENT TECHNIQUE

AMS is a highly sensitive method to search for small amounts of radionuclides in natural samples because it is able to fully suppress the interfering background from molecules of the same mass as the radionuclide of interest. For the determination of the ^{244}Pu abundance in bastnäsite, we used the TOF AMS setup at the Maier-Leibnitz-Laboratory in Garching [10,23].

The sample material was pressed into a graphite cathode, from which PuO^- molecules were extracted in the cesium sputter ion source.

On the low-energy side of the accelerator, negatively charged molecules of the correct mass were selected with the 90° injector magnet with a mass resolution of 1/200 and an additional energy selection was performed with an 18° electrostatic deflection.

A voltage of 11 MV was applied to the terminal of the MP tandem accelerator and the carbon stripper foil ($\approx 4 \mu\text{g}/\text{cm}^2$) in

the high-voltage terminal completely destroyed all molecules. Positive ions in high-charge states were produced and accelerated further on the high-energy side. For our experiment we selected the 11^+ charge state, so in total the plutonium ions reached energies around 130 MeV. The magnetic elements of the beam transport system were adjusted with $^{232}\text{Th}^{11+}$ from $^{232}\text{ThO}_2^-$ at correspondingly lower terminal voltage.

During the further beam setup on the high-energy side of the accelerator, the magnetic rigidity was kept constant. Between the measurements only the field of the injector magnet, the terminal voltage, and the voltage of a Wien velocity filter were adjusted to the different ions. After the tandem the charge state 11^+ was selected for plutonium by the Wien velocity filter and the high-resolution 90° analyzing magnet ($\frac{\Delta m}{m} \approx 3 \times 10^{-4}$) at a field strength of 1400 mT.

The ions were identified by means of a TOF spectrometer. The start signal was delivered by use of a microchannel plate array detecting the electrons released by the ions passing through a smooth $7 \mu\text{g}/\text{cm}^2$ carbon foil. An ionization chamber with a 0.9- μm -thick window and filled with 10 mbar isobutane determined the energy loss of the ions. A silicon surface barrier detector mounted at the end of the chamber simultaneously served for the residual energy measurement and for the stop signal. The TOF, two energy loss signals in the gas ionization chamber on a split anode, and the residual energy E_{res} in the surface barrier detector were recorded for particle identification.

All events from any nuclides not suppressed by the Wien velocity filter and the magnetic elements of the AMS setup were identified with respect to their mass-to-charge (A/q) ratio in the spectra.

Besides measuring ^{236}Pu and ^{244}Pu , we also tuned the system to $^{232}\text{Th}^{11+}$, $^{232}\text{Th}^{10+}$, and $^{235,238}\text{U}^{11+}$ to test the transmission of the accelerator and the detector response with respect to energy loss, residual energy, and TOF. $^{133}\text{Cs}^{6+}$ appears as an intense peak in the spectra (Figs. 1 and 2) for two reasons: it has an A/q ratio very similar to $^{244}\text{Pu}^{11+}$ and for this reason nearly the same TOF. Second, cesium ions are used to sputter the sample in the ion source and form a molecule of mass 260 in combination with ^{127}I . $^{133}\text{Cs}^{127}\text{I}$ cannot be separated from $^{244}\text{Pu}^{16}\text{O}$ on the low-energy side. Therefore, the counting rate for $^{133}\text{Cs}^{6+}$ had to be reduced by HNO_3 addition to remove iodine in the last chemical steps of the sample preparation described above.

The source was operated in a way that not more than 3000 events per second had to be recorded in the detector. But the large counting rate of $^{133}\text{Cs}^{6+}$ produced pileup events, which were also recorded. Pileup from more than two cesium events

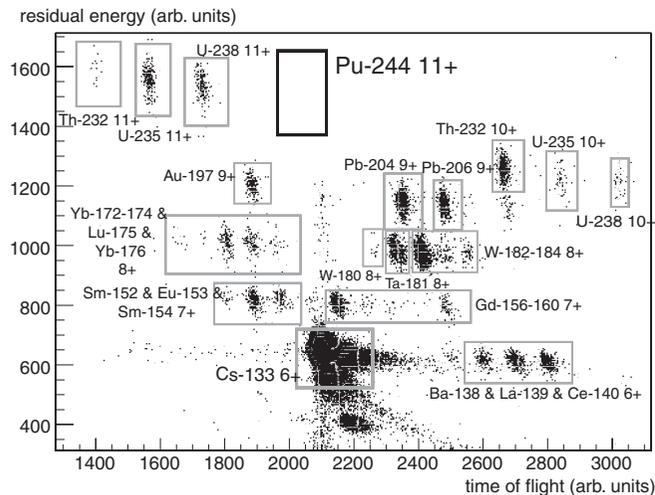


FIG. 1. Example of a TOF- E_{res} spectrum of a ^{244}Pu run from sample IH with a large number of well-separated background nuclides. Although cleaner spectra were also recorded, this one was chosen to illustrate the variety of well-identified background nuclides in the TOF spectrometer. The signal of the TOF and the silicon surface barrier detector are sufficient for the separation and no condition on the energy loss signals is required.

might be able to simulate a ^{244}Pu event in the residual energy. Such background events (Fig. 2) were identified in the data processing by electronic pileup recognition and by the analysis of the two ΔE signals because cesium and plutonium have a different energy loss in the gas ionization chamber.

Background from other nuclides is obviously not obscuring the ^{244}Pu region as can be seen in Figs. 1 and 2. The appearance of these various nuclides is not the same for all samples because the elements in the mineral's matrix were sometimes suppressed differently during the chemical

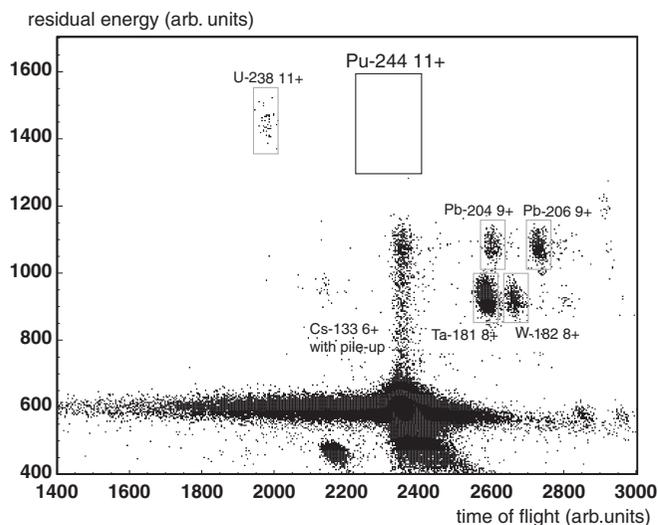


FIG. 2. Example of a TOF- E_{res} spectrum of a ^{244}Pu run from sample IJ with well-separated background nuclides. The event slightly below the expected range of ^{244}Pu most likely stems from threefold $^{133}\text{Cs}^{6+}$ pileup and vanishes after the application of the pileup rejection.

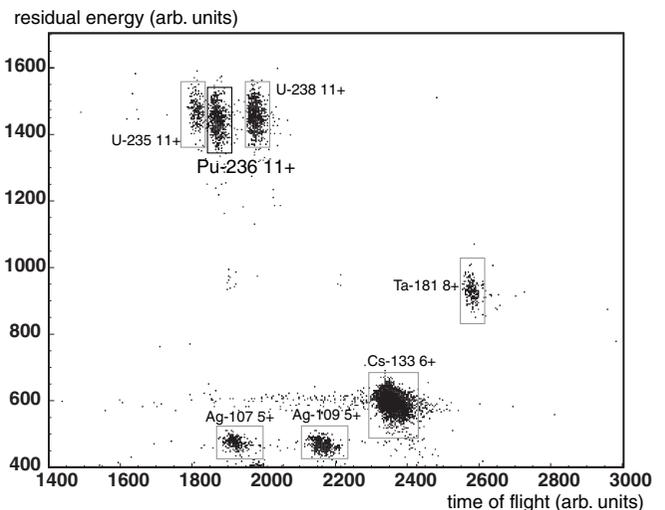


FIG. 3. Example of a TOF- E_{res} spectrum of a ^{236}Pu run from sample IJ.

processing. Only isotopes with a A/q ratio close to that of $^{244}\text{Pu}^{11+}$ ($\frac{\Delta A/q}{A/q} < 0.07$) appear in the spectra; others can be separated effectively by the Wien filter.

Typically once or twice every 2 h, the ^{236}Pu counting rate was measured to determine the efficiency (Fig. 3). The run time for ^{236}Pu lasted 2.5–5 min per normalization depending on the ^{236}Pu counting rate. The residual energy signal of ^{236}Pu is slightly shifted relative to the adjacent signals of ^{235}U and ^{238}U (Fig. 3). This is due to the larger energy loss of plutonium compared to uranium in the preceding ionization chamber and indicates that actually ^{236}Pu was measured for normalization. The average counting rate of two successive ^{236}Pu runs was scaled to the run time of the intermediate ^{244}Pu run to determine the yield of plutonium ions during the 244 run time. Therefore, the yield was determined for each sample independently (Table I).

For the normalization, it had to be taken into account that a larger dead time of the detector and the electronics occurred during the ^{244}Pu runs. These runs were affected by higher counting rates because of the ^{133}Cs interference.

A detection efficiency of one event (Table I) in the detector per 10^4 atoms in the sample can be reached with this setup.

Targets created from each 150-g sample were measured for several hours until the material was exhausted. At the end of the experiment, ^{244}Cm was used as the standard to determine the position of the signals for mass 244 in the TOF and the various energy-loss measurements (Fig. 4). These signals perfectly matched the expectations for the TOF signal obtained from our calculations based on the particular values of the reference isotopes for the beam tuning, i.e., ^{232}Th and ^{238}U , and of the reference isotope for the plutonium detection ^{236}Pu .

IV. RESULTS

The chemical processing was performed for five samples from the two lots of bastnäsite, each starting from 150 g mineral. No signal of ^{244}Pu could be detected during the measurements of the samples.

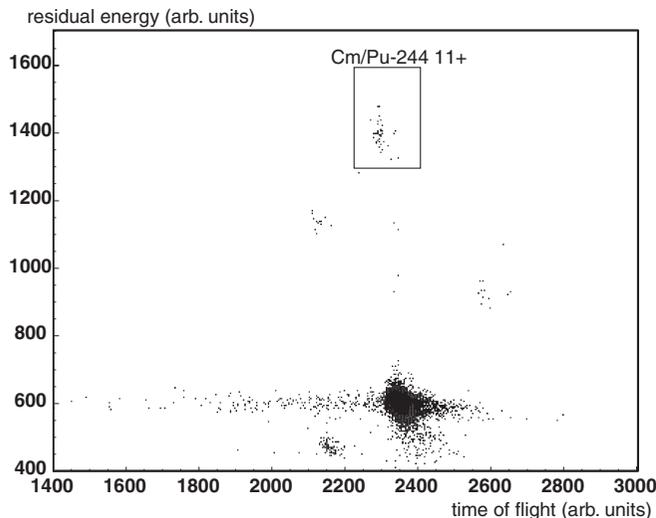


FIG. 4. TOF- E_{res} spectrum of the ^{244}Cm run following the measurement of sample IJ. The counts appear slightly lower in the E_{res} spectrum than expected for plutonium because of the larger Z of curium and its larger energy loss in the ionization chamber.

The overall efficiency (including chemical yield) for the total of all analyzed samples was 2.2×10^{-5} . This means that out of 10^6 plutonium atoms in the analyzed sample material 22 events would have been detected. For the 750 g of analyzed material, one count would be equivalent to a concentration of 61 atoms/g. The concentration C_{total} , which corresponds to one hypothetical count of ^{244}Pu found in the total measured sample material, is obtained from the one count equivalent concentrations C_i of the individual samples (Table I) in the following way:

$$C_{\text{total}} = \frac{1}{\sum_i \frac{1}{C_i}}. \quad (1)$$

We observed zero events during all our measurements. Therefore, we can only obtain an upper limit for the ^{244}Pu concentration in bastnäsite. This is done for each sample individually according to the statistical analysis of small signals [24] and further including uncertainties of the measurement technique. These amount to 5% due to the possible deviations in the transmission of the ^{244}Pu beam relative to the ^{236}Pu beam and to 5% due to the determination of the chemical yield. Each uncertainty is given as a 68.3% (1σ) confidence level (C.L.). With zero counts of ^{244}Pu measured for each sample, at 99% confidence level the upper limit is 4.74 events [24]. The individual upper limits calculated for each sample result in the total upper limit according to Eq. (1).

At 99% confidence level, the upper limit amounts to 370 atoms or 1.5×10^{-19} g ^{244}Pu per gram bastnäsite. Relative to the uranium and thorium content in the mineral, which was determined by α spectrometry, this means a maximum concentration of $^{244}\text{Pu}/^{238}\text{U} = 1.7 \times 10^{-15}$ and $^{244}\text{Pu}/^{232}\text{Th} = 1.0 \times 10^{-16}$, respectively.

V. ABUNDANCE ESTIMATION FOR ^{244}Pu

The initial ratio of $(^{244}\text{Pu}/^{238}\text{U})_0$ at the time of the Solar System formation 4.57 Ga ago has been recently determined to

be 0.008 from the measurement of a fissionogenic xenon excess in meteorites and in 4.1–4.2 billion-year-old zircons [25,26]. ^{244}Pu decayed to a fraction of 1.1×10^{-17} since the formation of these minerals, the ^{238}U in the same time span decayed to 49% of the initial value. Today, the ratio of $^{244}\text{Pu}/^{238}\text{U}$ in a perfectly conserved mineral should be on the order of 2×10^{-19} . For the estimation of this value, the uncertainty of the ^{244}Pu half-life is negligible compared to the uncertainty of the age determination of the zircons.

Because of the homologous behavior of plutonium and the rare-earth elements, plutonium and these elements may be considered to be enriched similarly in rare-earth minerals relative to the abundance in Earth's crust. For the following calculations, we compare the contents of cerium and uranium of the bastnäsite used in this study. Samarium and plutonium are chemical homologs as both have six electrons in the $4f$ or $5f$ shell, respectively. Jones and Burnett [27] found a geochemical coherence of plutonium and light rare-earth elements in reducing environments of meteoritic material with only little fractionation between plutonium and samarium. They also suggested that the coherence of plutonium with cerium or neodymium in igneous processes would be even better. The homologous behavior of plutonium and neodymium had been studied earlier for different phases of meteoritic formation [28,29]. Further, CeO_2 was shown to behave homologous to plutonium [30]. Because of the similar chemical behavior of cerium and plutonium and the especially strong enrichment of cerium in bastnäsite (~ 5400 -fold), this element was chosen to estimate an upper limit for the plutonium abundance in the sample material.

Assuming a similar enrichment of cerium and plutonium, the latter would be also ~ 5400 times more abundant in bastnäsite than in Earth's crust. In contrast, uranium in this mineral is only enriched by a factor of about 40. In comparison to that in Earth's crust, in bastnäsite the abundance of plutonium relative to uranium is then expected to be higher by a factor of 135. For this reason, an upper limit of the $^{244}\text{Pu}/^{238}\text{U}$ ratio in this mineral can be estimated to 3×10^{-17} .

VI. CONCLUSION

In our attempt to detect primordial ^{244}Pu we could prove that the TOF AMS setup at the MLL is capable of highly sensitive and background-free determinations of this radionuclide in natural materials. Our upper limit of 370 atoms ^{244}Pu per gram bastnäsite at 99% C.L. is lower than the abundance given by Hoffman *et al.* [4]. A concentration of about 2350 atoms ^{244}Pu per gram bastnäsite had been found in this previous study, with a lower limit of 1500 atoms ^{244}Pu per gram due to blank corrections. Based on our new results a homogeneous distribution of ^{244}Pu in this mineral at such a high level has to be excluded. The bastnäsite samples of Ref. [4] and our study are from the same mine and have a similar abundance of cerium, which is considered to be a homolog element to plutonium. Therefore, such large variations of the ^{244}Pu content in the material are not very likely, but seem to be the only way to reconcile our result with that of Hoffman *et al.* [4].

If, however, the assumption of a similar enrichment of the homologs plutonium and cerium in bastnäsite were right,

our estimation of the ratio $^{244}\text{Pu}/^{238}\text{U}$ in this mineral would suggest that the average abundance even could be 60-fold lower than our limit of $^{244}\text{Pu}/^{238}\text{U} < 1.7 \times 10^{-15}$. The way toward a future positive detection of smallest traces of ^{244}Pu then only could be to search in larger amounts of bastnäsité in an experiment with constant and high yields of both chemical processing and mass-spectrometry measurement.

Another mineral, in which one can expect ^{244}Pu to be more abundant than in bastnäsité, is monazite, especially enriched in rare earths and also in thorium. Nonetheless, the unknown path of plutonium during the geochemical development makes predictions about the best target mineral difficult.

The direct detection of primordial ^{244}Pu on Earth therefore remains problematic.

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