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Direct search for primordial ^{244}Pu in Bayan Obo bastnaesite

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ABSTRACT

The abundances of heavy elements produced in r-process nucleosynthesis in the early solar system need experimental verification. ^{244}Pu could be the heaviest primordial nuclide produced before the formation of the Earth still being detectable today. As recent attempts failed to confirm the discovery of ^{244}Pu signals at a concentration of 1.0×10^{-18} g/g in bastnaesite reported by Hoffman *et al.* in this study, the total primordial ^{244}Pu in 450 g bastnaesite sample from Bayan Obo ore (China) was measured using ultra-sensitive compact accelerator mass spectrometry (AMS). As no ^{244}Pu signal was detected, an upper limit for the ^{244}Pu in our bastnaesite sample was estimated to be 2.1×10^{-20} g/g at 99% confidence level.

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Plutonium-244 (^{244}Pu), with a half-life of 81.1 ± 0.3 Myr [1], could only be produced in the rapid neutron-capture process (r-process) under the high neutron density and high-temperature stellar environment. ^{244}Pu could be the heaviest and the shortest-lived pure r-process primordial nuclide that may still remain detectable on Earth [2]. There is natural and anthropogenic ^{244}Pu on Earth, and the natural ^{244}Pu is produced only through r-process and can be classified into primordial and live interstellar. The primordial ^{244}Pu is supposed to be produced in the stellar evolution during the formation of the Earth, and the existence of which has been indirectly proven by precise measurement of excessive ^{244}Pu-fissiogenic xenon isotopes found in achondritic meteorites [3]. The initial abundance ratio of ^{244}Pu to ^{238}U for early Solar System ((^{244}Pu/^{238}U)$_{\mathrm{ESS}}$) was estimated to be ~0.008 from Xe isotopic loss in ancient zircon samples [4]. In the past millions of years, the interstellar medium (ISM, composing of diffused gas clouds and small solid particles) ejected by supernova explosion near the solar system could contain the live interstellar ^{244}Pu, which may eventually be deposited on Earth and buried in ocean floor with the ejected ISM dust particles [5]. In addition, anthropogenic ^{244}Pu can be produced in high flux reactors and thermonuclear detonation events, and it was only found at very low levels (with a ^{244}Pu/^{239}Pu ratio of approximately $(5.7 \pm 1.0) \times 10^{-5}$ in the top layers of surface soil and sediment samples [6].

In recent years, the flux and accumulation rate of live interstellar ^{244}Pu in sediment and deep-sea iron-manganese encrustation were analyzed to estimate the frequency of r-process and to explain the mechanism of stellar evolution [5,7,8]. Due to very similar chemical properties between actinides and lanthanides, primordial ^{244}Pu is most likely to be enriched and thus found in rare earth minerals. Several attempts have been made to search for primordial ^{244}Pu in rare earth samples, including bastnaesite and gadolinite samples, for verification of its abundance produced in the formation of the solar system [9–11], especially its ratio to heavy nuclides, which is an important parameter for validating the theories and models of galactic nucleosynthesis, chronology of solar system and terrestrial evolution. In 1971, the content of ^{244}Pu had been first reported to be 1×10^{-18} g/g in a bastnaesite sample obtained from the Mountain Pass Mine (California, USA) by Hoffman and Lawrence [1]. However, subsequent studies for searching such a ^{244}Pu signal, either *via* indirect method [12] by searching the fission tracks of ^{244}Pu or *via* direct detection [10] of ^{244}Pu with an upper limit of 10 folds lower than Hoffman's, failed to confirm the concentration of ^{244}Pu reported by Hoffman and Lawrence. It should also be noted that the bastnaesite samples used in the previous direct detection of ^{244}Pu [1,9,10] were not completely dissolved and measured, which could lead to under-estimation of the ^{244}Pu results. Thus, in the earlier study, we have developed an ultra-sensitive analytical method for measuring total ^{244}Pu in

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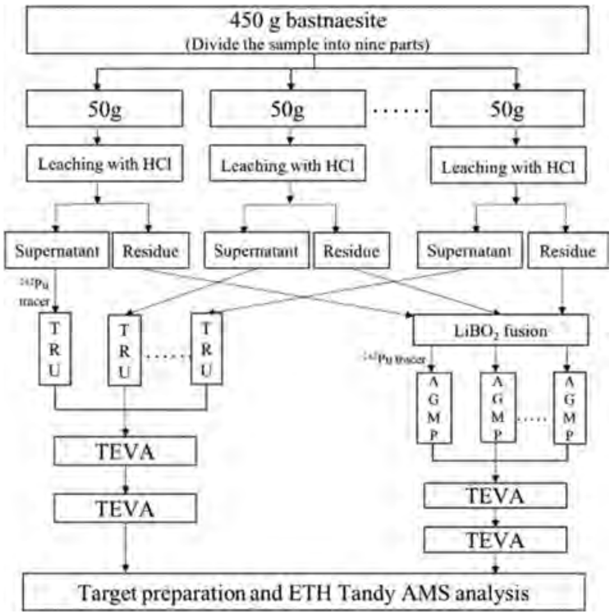

Fig. 1. Flow diagram of the sample preparation procedure.

completely digested bastnaesite samples by accelerator mass spectrometry (AMS) [11]. For complete dissolution of 22.27 g bastnaesite concentrate sample, an upper limit of ~4.5×10^{-19} g/g ^{244}Pu was obtained at 99% confidence level, which still disapproved the detection value reported in the reference [1]. Therefore, a larger bulk sample need to be processed to verify the abundance of primordial ^{244}Pu.

In this work, the abundance of ^{244}Pu in 450 g of bastnaesite concentrate sample from the Bayan Obo ore deposit is measured using the ultra-sensitive AMS method developed previously [11]. The enrichment factor and the abundance of ^{244}Pu are estimated, and the acid leaching behavior of Pu is discussed.

The direct detection of primordial ^{244}Pu in terrestrial samples would be extremely difficult as it should have decayed to an almost immeasurable fraction (1.1×10^{-17}) of its initial abundance. Owing to the processes of geochemical enrichment, the abundance of an element in a favourable host mineral can exceed its average terrestrial abundance by a large (enrichment) factor. Primordial ^{244}Pu is most likely to be enriched in rare earth mineral samples because of the similar chemical properties of actinides and lanthanides. The bastnaesite sample used in the present study was derived from the Bayan Obo deposit (China) formed in Mesoproterozoic Era about 1.3 Ga ago. The principle rare earth minerals are bastnaesite ($REFCO_3$) and monazite ($REPO_4$) with the ratio of about 9:1 to 1:1, and the total REO content in the sample was determined to be 49.3% [13]. ^{239}Pu and ^{240}Pu in this bastnaesite concentrate sample was measured to be not above 0.1 fg/g level, confirming that the sample used in the present study has not been contaminated by anthropogenic Pu.

A set of samples, including one 450 g and one 50 g bastnaesite concentrate sample as well as two of procedural blank samples, were analyzed. A flow diagram of the sample preparation procedure is given in Fig. 1. The 450 g sample was divided into nine of ~50 g samples for pretreatment and the first stage column separation, all the eluate samples were then mixed together for the subsequent TEVA resin purification. The details of the column separation and purification method have been described elsewhere [11]. For the sample preparation, the bastnaesite concentrate samples were firstly leached by 12 mol/L HCl, and the supernatant solution and the residue were obtained, respectively. About 70% of the REEs and 9% of the Th dissolved in the HCl leachate, while ~90% of Th and ~30% of REEs remained in the residue fraction. The residue was dried and mixed well with lithium metaborate, lithium iodide and sodium persulfate, and fused at 950 °C. The fusion button was dissolved in mixed acid (6 mol/L HCl + 4 mol/L HNO_3). About 1–2 pg of the ^{242}Pu tracer was added to the HCl leachate and the solution of the fusion button for tracing the chemical recovery, and nine parts of the 450 g sample were added with 200 fg of the ^{242}Pu, and the two solutions were then separately processed. For Pu separation and purification of the HCl leachate, a TRU column was used to directly extract Pu in the HCl leachate, and Pu in the eluate was further purified using the TEVA column repeatedly to remove residual REE and Th. For the separation and purification of the bastnaesite residue solution, NaOH was added to co-precipitate Pu with REE hydroxide. The precipitate was dissolved with HCl, and Pu was separated using an AGMP-1 M anion resin column. The eluate from the AGMP-1 M column was also purified with the TEVA resin repeatedly. The AMS target was then prepared for the TEVA eluate sample using mixed titanium and iron hydroxide co-precipitation method with 0.4 mg of Ti and 0.1 mg of Fe [14]. The Fe/Ti hydroxide precipitate was subsequently baked at 650 °C for conversion to the oxide form. The oxide sample was finally mixed with niobium powder and pressed into a Ti target holder for AMS measurement.

The isotopic ratios of the analytes to the tracer (*i.e.*, ^{239}Pu/^{242}Pu and ^{244}Pu/^{242}Pu) in the HCl leachate and the residue of these bastnaesite concentrate samples were measured by the low energy (300 kV) AMS system TANDY at ETH Zurich [15]. This compact AMS was built in late 1990s, and the system had been significantly modified in order to improve its performance, including a new gas ionization detector, an upgraded ion source, a second HE magnet, and the implementation of He stripping [16], which significantly increased the overall transmission for actinides [15]. Also the AMS target preparation method had been effectively optimized, which further improved analytical accuracy and precision [17].

The details of the AMS setup for the measurements of actinides have been described elsewhere [14,18]. To achieve lower ^{244}Pu detection limits, each sample target has been measured for ~6.5 h and nearly sputtered until exhaustion. Only the contents of ^{239}Pu and ^{244}Pu were analyzed in the present study, and a large portion of the AMS measurement time was allocated to ^{244}Pu (62.5%) to achieve the possibly lowest detection limits for ^{244}Pu. Good and consistent total efficiencies were obtained for the HCl leachates and the residues of the two bastnaesite concentrate samples (450 and 50 g), but the efficiencies for the procedural blank samples were significantly lower, which may be due to a loss of Pu in the column separation. The total efficiencies (chemical yield included) of Pu isotopes in the present study were respectively 2.40×10^{-4} for the HCl leachate and 4.20×10^{-4} for the residue of the 450 g sample, which were ~20 times higher than the achieved total efficiency of ^{244}Pu (2.2×10^{-5}) reported by Lachner *et al.* [10].

Although the main sources of ^{239}Pu in the environment are anthropogenic, small amounts of ^{239}Pu can be produced naturally *via* neutron capture on ^{238}U [19], and the occurrence of natural ^{239}Pu was subsequently demonstrated in uranium ores by a series of studies [20,21]. The ratio of ^{239}Pu/^{238}U has been estimated to be $(0.1–3) \times 10^{-12}$ in uranium ore samples [21]. The natural ^{239}Pu content in our bastnaesite samples can thus be calculated to be $(0.19–5.7) \times 10^{-18}$ g/g taking into account the ^{238}U content measured by alpha spectrometry (1.90×10^{-6} g/g). As most of the Th (>90%) retained in the residue after leaching with concentrated HCl [11], it would be skeptical that the Pu, which is also stable at +4 valence with very similar chemical properties to Th(IV), may not be fully released by acid leaching. In order to verify the necessity of complete dissolution of the sample and measurement of ^{244}Pu in the leaching residue, the two sample fractions (*i.e.*, the HCl

Table 1
Results for ^{239}Pu in bastnaesite concentrate samples and reagent blanks.

No.	Sample description	^{242}Pu tracer (fg)	Counts[a] (amu 242)	Counts[a] (amu 239)	Measured 239/242 ($\times 10^{-3}$)	Blank corrected 239/242 ($\times 10^{-3}$)[b]	^{239}Pu conc. (bl corr) (ag/g)
RE1101–1S	HCl leachate of 450 g sample	1718.4	171,198	88	0.51 ± 0.05	0.4 ± 0.05	1.49 ± 0.17
RE1101–1R	Residue of 450 g sample	1360.5	237, 247	464	1.95 ± 0.09	1.87 ± 0.09	5.57 ± 0.26
RE1101–2S	Leachate of 50 g sample	1085.0	208, 312	10	0.05 ± 0.02	–	–
RE1101–2R	Residue of 50 g sample	801.6	133, 216	45	0.34 ± 0.05	0.19 ± 0.03	2.97 ± 0.51
RE1101-B1S	Blank of leachate sample [c]	1087.3	1858	21			
RE1101-B1R	Blank of residue sample	791.8	17, 217	16			
RE1101-B2S	Blank of leachate sample	1092.9	2811	19			
RE1101-B2R	Blank of residue sample	794.6	905	12			

[a] Both the amu 239 and amu 242 were measured for about 3635 s.
[b] Only the counts of blank samples was used for correction.
[c] The procedural blank sample corresponded to the 50 g sample.

leachate and the digested solution of the residue) were processed separately, and the contents of ^{239}Pu were analyzed. The masses of ^{239}Pu were calculated from the measured and blank corrected atomic ratios of ^{239}Pu to the known amounts of ^{242}Pu added as tracer. The ^{239}Pu for the HCl leachates and the residue solutions of the bastnaesite samples are listed in Table 1.

Attogram level of ^{239}Pu were detected in the AMS targets of both bastnaesite samples, and the counting rates of ^{239}Pu in the 450 g sample are ~9 and 10 times higher than those of the 50 g sample, which obviously correlated with the amount of sample or the reagent used. Since the counting rate of ^{239}Pu in the residue sample was ~4.5 times higher than that of the HCl leachate sample, ^{239}Pu may come from two sources. One possibility was that the ^{239}Pu came from the reagents used in the sample preparation procedure (particularly $LiBO_2$ for the fusion of the residue and NaOH for the coprecipitation step). The other source was indeed the presence of natural ^{239}Pu in the bastnaesite sample, implying that majority (>70%) of the natural Pu may still retained in the residue (similar to Th) after leaching with HCl. Then, in the future studies, the rare earth sample needs be completely dissolved to ensure that the ^{244}Pu content is not under-estimated; meanwhile, it also suggests that the samples containing a high Th content could be more suitable for searching primordial ^{244}Pu due to the very close chemical behaviors of these two elements [11]. Unfortunately, due to the poor chemical recoveries of the procedural blanks, the content of ^{239}Pu in the blank samples could not be accurately measured, and possible contributions of ^{239}Pu from the chemical reagents used in the sample preparation procedure could not be completely excluded. As a consequence, it is not appropriate to use the ^{239}Pu/^{242}Pu ratio of the blanks to correct the samples for the ^{239}Pu contamination because this method assumes that all ^{239}Pu had been introduced together with the ^{242}Pu tracer. Instead, we used the average counting rate of ^{239}Pu from the blank samples for correction. Still, the origin of ^{239}Pu in the sample needs to be further analyzed and verified. Even if ^{239}Pu came from the Global Fallout contamination, since the maximum contamination level ^{244}Pu/^{239}Pu ratio is 1×10^{-5} [22], the maximum level of ^{244}Pu from Global Fallout in our sample were not excess 5×10^{-23} g/g, which is significantly lower than the expected range of primordial ^{244}Pu in the rare earth minerals (Fig. 2).

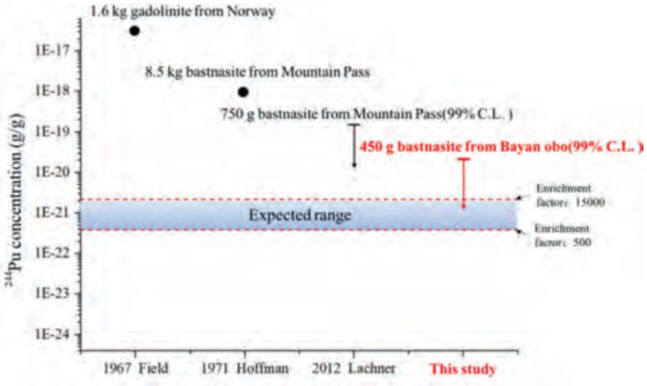

Fig. 2. Comparison of analytical concentration of ^{244}Pu in rare earth mine.

For the ^{244}Pu measurement in bastnaesite concentrate, no ^{244}Pu signal was detectable for all the HCl leachate and the residue samples. Based on the total efficiency of Pu, one count of ^{244}Pu in the 450 g sample would equal to 5.6×10^{-21} g/g and 3.2×10^{-21} g/g for the HCl leachate and the residue, respectively. This means, if there were 14 ^{244}Pu atoms for the HCl leachate or 8 ^{244}Pu atoms for the residue contained in one gram of bastnaesite concentrate, a ^{244}Pu signal would have been detected. An upper detection limit (UDL) for the ^{244}Pu content in the HCl leachate or the residue of the bastnaesite concentrate can be estimated (Table 1) using the equation below:

$$\mathrm{UDL} = (\mu \times 244)/(\mathrm{N_A} \times \mathrm{m_i} \times \varepsilon_{244})$$

where μ is the upper limit counts at 99% C.L., corresponding to 4.74 counts for a sample with zero background and zero count observed [23]; N_A is the Avogadro constant (*i.e.*, 6.022×10^{23}); $\mathrm{m_i}$ is the bastnaesite mass processed for individual sample; and ε_{244} is the total ^{244}Pu efficiency for individual sample (Table 2).

The upper detection limits were calculated to be 1.8×10^{-20} g ^{244}Pu and 1.0×10^{-20} g ^{244}Pu per gram bastnaesite for the HCl leachate and the residue of the 450 g sample at 99% confidence level, respectively. Thus, the upper detection limit of ^{244}Pu in total bastnaesite concentrate at 99% confidence level is 2.1×10^{-20} g/g, calculating by combined upper detection limits of the HCl leachate and the residue (*i.e.*, $\sqrt{(1.8^2 + 1.0^2)} \times 10^{-20}$). This upper limit is nearly 7 times lower than the lowest upper limit of ^{244}Pu (1.5×10^{-19} g/g of ^{244}Pu measured in 750 g bastnaesite sample, Fig. 2) in a bastnaesite sample previously reported by Lachner *et al.* [10]. This confirms that the claimed discovery of a higher ^{244}Pu concentration in bastnasite concentrate (1×10^{-18} g/g of ^{244}Pu) may not be the primordial signal.

Estimation of ^{244}Pu abundance. The initial (^{244}Pu/^{238}U)$_{ESS}$ abundance ratio in the early formation of the solar system 4.57 billion years ago has been determined to be ~0.008 from the measurements of a fissiogenic xenon excess in meteorites and in 4.1–4.2 billion-year-old zircons. Due to the radioactive decay of the ^{238}U and ^{244}Pu, the existing ^{244}Pu on earth has decayed to a fraction of 1.1×10^{-17} to its initial concentration since the formation of the solar system and ^{238}U reduced by half. Then, the present abundance ratio of primordial ^{244}Pu/^{238}U is expected to be around 1.6×10^{-19} in terrestrial samples. The upper limit of the ^{244}Pu content in the Earth's crust is deduced to be 4×10^{-25} g/g from the upper continental crust abundance of ^{238}U (*i.e.*, 2.5×10^{-6} g/g) [24]. Owing

Table 2
Results for ^{244}Pu in bastnaesite concentrate samples and reagent blanks.

Sample ID	Bastnaesite mass (g)	Total efficiency[a]	One count equiv. (^{244}Pu atoms)	Upper limit for ^{244}Pu[b] (g/g bastnaesite)
HCl leachate samples				
REE1101–1-S	450	2.40×10^{-4}	4.16×10^{3}	1.8×10^{-20}
REE1101–2-S	50	4.63×10^{-4}	2.16×10^{3}	8.3×10^{-20}
RE1101-B1S	Blank	4.12×10^{-6}	2.43×10^{5}	
RE1101-B2S	Blank	6.20×10^{-6}	1.61×10^{5}	
Residue samples				
REE1101–1-R	450	4.20×10^{-4}	2.38×10^{3}	1.0×10^{-20}
REE1101–2-R	50	4.01×10^{-4}	2.50×10^{3}	9.6×10^{-20}
RE1101-B1R	Blank	5.24×10^{-5}	1.91×10^{4}	
RE1101-B2R	Blank	2.75×10^{-6}	3.64×10^{5}	

[a] The total efficiency (chemical yield included) was calculated by dividing the overall efficiency of ^{242}Pu over the proportion of amu 242 measurement time; while the overall efficiency of ^{242}Pu is obtained by dividing the total measured counts of ^{242}Pu over the total ^{242}Pu atoms initially added into the sample.

[b] The upper limit for ^{244}Pu was calculated by the upper limit counts of amu 244 at 99% C.L., it would be 4.74 counts for a sample with zero count observed and zero count of background.

Table 3
Estimated upper limits of ^{244}Pu refer to the enrichment factor of Th and Ce in the bastnaesite mineral.

Initial $(^{244}Pu/^{238}U)_{ESS}$ abundance ratio [4]	0.008	
^{244}Pu/^{238}U in terrestrial sample	1.6×10^{-19}	
Upper continental crust abundance of ^{238}U (g/g)	2.5×10^{-6}	
Upper continental crust abundance of ^{244}Pu (g/g)[a]	4×10^{-25}	
	^{244}Pu Enriched with	
	^{232}Th	Ce
Measured in this bastnaesite (g/g) [11]	1.67×10^{-3}	0.199
Upper continental crust abundance (g/g)	1.03×10^{-5}	6.57×10^{-5}
Enrichment factor to crust	1.62×10^{2}	3.03×10^{3}
Expected ^{244}Pu content (g/g)	6.5×10^{-23}	1.2×10^{-21}
Upper detection limit of ^{244}Pu (g/g)	2.1×10^{-20}	

[a] The upper continental crust abundance of ^{244}Pu was calculated by multiplying the ^{244}Pu/^{238}U in the terrestrial sample by the upper continental crust abundance of ^{238}U.

to geochemical enrichment processes, the abundance of ^{244}Pu in a rare earth mineral can exceed its average terrestrial abundance by a large enrichment factor. However, due to the uncertainty of plutonium oxidation state during high-temperature geological history of rare earth ore bodies, it would be difficult to accurately estimate this enrichment factor. Since the most stable oxidation states of Pu are tetravalent and trivalent, plutonium is very likely to be enriched in tetravalent state with thorium(IV) and cerium(IV) in the oxidizing environment, and concentrated with trivalent rare earth elements in reducing environment.

Wedepohl [24] reported that the discrete ratios of fissiogenic xenon components of ^{244}Pu in an ancient igneous rock seemed closely associated with the light REEs. CeO_2 has been often used as a surrogate for PuO_2 when studying ZrO_2-MgO matrix nuclear fuel containing PuO_2 [25]. Jones and Burnett [26] reported that Pu and light REE (especially cerium) in meteorite material were almost geochemically identical in reducing environment with very little fractionation. Thus, cerium could be a chemical and structural homologue of plutonium, and their trivalent and tetravalent oxide species could be enriched concurrently in geological environment. Using the similar enrichment factor of Pu to Ce, the upper limit of ^{244}Pu content in this bastnasite sample can be calculated as 1.2×10^{-21} g/g, *i.e.*, the product of the crustal abundance of ^{244}Pu and the enrichment factor of Ce (3.03×10^{3}, measured by XRF analysis) (Table 3). Thus, the upper detection limit (UDL) of ^{244}Pu in 450 g rare earth concentrate (2.1×10^{-20} g/g) is still ~18 folds higher than the expected ^{244}Pu content in this bastnaesite according to the initial $(^{244}Pu/^{238}U)_{ESS}$ abundance ratio of 0.008. The UDL still needs to be pushed down further to detect the primordial ^{244}Pu and to verify whether or not the initial abundance ratio is correct. However, it would be a great analytical challenge as 8 kg of the present bastnaesite concentrate sample is required to be processed. With such an increase of sample volume, it is difficult to ensure the high chemical recovery and low background of Pu.

According to genetic mineralogy and minerocoenology, mineral symbiosis follows the principle of isomorphism, which means that the positions of some ions, atoms or molecules in the crystal structure are occupied by the others with similar properties. Compared to Ce^{4+} and Ce_2O_3, the radius of Pu^{4+} ion is even closer to that of the Th^{4+} ion, and the melting point of PuO_2 is also similar to that of ThO_2. Therefore, the behavior of Pu in rare earth minerals may be more similar to Th in the long process of geological evolution. Then, the expected ^{244}Pu content in this bastnaesite sample is calculated to be 6.5×10^{-23} g/g by multiplying the upper crustal abundance of ^{244}Pu with the enrichment factor of Th (162, measured by XRF analysis [11]). As the upper detection limit of ^{244}Pu achieved for 450 g rare earth concentrate is 2.1×10^{-20} g/g, the direct detection of primordial ^{244}Pu in this sample seems insurmountably difficult. The enrichment factor of plutonium in any rare earth mineral seems unlikely to significantly exceed the maximum enrichment of Th (2×10^{7}) and rare earth elements (3×10^{5}) in its richest mineral [9]. Other samples with high concentrations of Th, such as monazite and gadolinite concentrate, would probably be the best candidates for a positive detection of primordial ^{244}Pu in nature. Alternatively, with more detailed studies of the differentiation ratio of Pu/Th in rare earth extraction process for correction of the content of primordial ^{244}Pu, sample volume could be reduced by analyzing the highly concentrated Th residue samples from processing monazite for extraction of REEs.

In summary, the measurement of ^{244}Pu in the HCl leachate and residue of 450 g of Bayan Obo bastnaesite concentrate was performed using the complete digestion ultra-sensitive analytical method, for attempting to verify the initial $(^{244}Pu/^{238}U)_{ESS}$ abundance ratio in the early formation of the solar system. Attogram level of ^{239}Pu was found in the sample target, and the counting rate of ^{239}Pu in the residue was ~4.5 times higher than that in the HCl leachate, which imply that Pu could preferentially concentrate in its tetravalent state with Th(IV) in the bastnaesite. Since no true signal of ^{244}Pu was observed, an upper detection limit for the ^{244}Pu content in our bastnaesite concentrate sample was estimated to be 2.1×10^{-20} g/g at 99% confidence level, which is the lowest upper limit obtained so far. This result denies the discovery of 1.0×10^{-18} g/g primordial ^{244}Pu in bastnaesite reported by Hoffman and Lawrence. The possible upper limit of ^{244}Pu content in our sample was estimated to be in the range of 1.2×10^{-21} g/g and 6.5×10^{-23} g/g by assuming the same enrichment factor of Pu as cerium or thorium, respectively. Therefore, it would still be problematic for direct search of primordial ^{244}Pu in terrestrial samples even if a much larger size of this sample is processed. Samples with high concentrations of Th could be the most promising choice for the future study.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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References

[1] D.C. Hoffman, F.O. Lawrence, Nature 234 (1971) 132–134.
[2] S. Goriely, G. Martinez-Pinedo, Nucl. Phys. 944 (2015) 158–176.
[3] J. Kunz, T. Staudacher, C.J. Allegre, Science 280 (1998) 877–880.
[4] G. Turner, A. Busfield, S. Crowther, et al., Earth Planet. Sci. Lett. 261 (2007) 491–499.
[5] A. Wallner, T. Faestermann, J. Feige, et al., Nat. Commun. 6 (2015) 1–9.
[6] P. Steier, E. Hrnecek, A. Priller, et al., Nucl. Nucl. Inst. Methods Phys. Res. B 294 (2013) 160–164.
[7] A. Wallner, M.B. Froehlich, M.A.C. Hotchkis, et al., Science 372 (2021) 742–745.
[8] G. Raisbeck, T. Tran, D. Lunney, et al., Nucl. Inst. Methods Phys. Res. B 259 (2007) 673–676.
[9] P.R. Fields, A.M. Friedman, J. Milsted, et al., Nature 212 (1966) 131–134.
[10] J. Lachner, I. Dillmann, T. Faestermann, et al., Phys. Rev. C 85 (2012) 1–6.
[11] Y. Wu, X.X. Dai, M. Christl, et al., ACS Earth Space Chem. 5 (2021) 1316–1324.
[12] E.C. Alexander, Science 172 (1971) 837–840.
[13] M. Li, X.W. Zhang, Z.G. Liu, et al., Rare Met. 32 (2013) 312–317.
[14] M. Christl, X.X. Dai, J. Lachner, et al., Nucl. Inst. Methods Phys. Res. B 331 (2014) 225–232.
[15] M. Christl, C. Vockenhuber, P.W. Kubik, et al., Nucl. Inst. Methods Phys. Res. B 294 (2013) 29–38.
[16] C. Vockenhuber, V. Alfimov, M. Christl, et al., Nucl. Inst. Methods Phys. Res. B 294 (2013) 382–386.
[17] X.X. Dai, M. Christl, S. Kramer-Tremblay, et al., Anal. Chem. 88 (2016) 2832–2837.
[18] H.A. Synal, Int. J. Mass Spectrom. 349-350 (2013) 192–202.
[19] K.M. Wilcken, T.T. Barrows, L.K. Fifield, et al., Nucl. Inst. Methods Phys. Res. 259 (2017) 727–732.
[20] G.T. Seaborg, M.L. Pearlman, J. Am. Chem. Soc. 70 (1948) 1571.
[21] C.A. Levine, G.T. Seaborg, J. Am. Chem. Soc. 73 (1951) 3276.
[22] C. Tighe, M. Castrillejo, M. Christl, et al., Nat. Commun. 12 (2021) 1381.
[23] G.J. Feldman, R.D. Cousins, Phys. Rev. D 57 (1998) 3873–3889.
[24] K.H. Wedepohl, Cosmochim. Acta 59 (1995) 1217–1232.
[25] K. Holliday, T. Hartmann, K.J. Czerwinski, Nucl. Mater. 392 (2009) 487–493.
[26] J.H. Jones, D.S. Burnett, Geochim. Cosmochim. Acta 51 (1987) 769–782.