



Characterization of meteoric ^{10}Be in certified reference materials for use in internal control standards

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Abstract

In recent decades, interest in the measurement of ^{10}Be has increased due to its relevance in various fields of science. Trace amounts of ^{10}Be produced from meteoric sources require sensitive accelerator mass spectrometry (AMS) measurements and robust sample preparation. The extraction, separation, and preparation of the appropriate oxide form for AMS require extensive and careful laboratory processing and certified reference materials to validate the chemical performance of the protocols used and the calibration of the AMS system in the measurement. In this work, the meteoric ^{10}Be concentrations in two certified reference materials are characterized to establish their suitability as internal control standards for laboratory chemical preparation and AMS measurements of this radioisotope in our laboratory and the whole AMS community.

Keywords ^{10}Be meteoric concentration · Cosmogenic isotopes · Sediments · Soils · AMS

Introduction

^{10}Be is an ideal nuclide for numerous investigations in geosciences and cosmosciences, astrophysics, and nuclear sciences [1]. Meteoritic ^{10}Be is a long-lived radionuclide (half-life = 1.38 ± 0.01 million years [2]) of beryllium formed in the upper atmosphere by the interaction of cosmic rays with the main component of the atmosphere: nitrogen and oxygen [3].

^{10}Be has found a wide range of applications in many fields of science [3–10] and, after ^{14}C , is the most measured radioisotope by AMS [11]. In recent years, more than 30,000

^{10}Be samples have been measured by AMS worldwide. The advent of AMS [12, 13] has significantly improved detection sensitivity by several orders of magnitude, reducing sample size and the time required for sample preparation and analysis. Even though AMS is the most sensitive technique and, in some cases, the only option to quantify ^{10}Be concentrations, it is essential to have tools that allow the validation and verification of results to carry out rigorous and reliable investigations [11]. Certified reference materials (CRMs), also known as laboratory standards, play a crucial role in this process by providing points of comparison and calibration for measurements and analysis [14]. CRMs have been recognized worldwide, and their use has become essential in ensuring the quality, safety, and reliability of measurements in various applications. With the development of more advanced analytical techniques, such as mass spectrometry and high-resolution spectroscopy, the accuracy and traceability of CRMs have improved. Few CRMs have determined the concentration of ^{10}Be to validate its measurement by AMS. NIST ^{10}Be SRM-4325 offers certified values of the $^{10}\text{Be}/^9\text{Be}$ isotope ratio but is no longer available, and CoQtz-N: a quartz reference material for in-situ ^{10}Be determination. Currently, no reference material certifies the meteoric ^{10}Be concentration. In this sense, the characterization of the meteoric ^{10}Be in two different IAEA CRMs is proposed for use as an internal control standard in routine radiochemical processes at AMS Facilities.

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Experimental

The characterization of meteoric ^{10}Be concentration in the International Atomic Energy Agency (IAEA) certified reference materials Soil-6 and 385, which have been used to certify artificial radioisotopes, usually from nuclear accidents, was carried out.

Certified reference material Soil-6

The soil (topsoil to a depth of 10 cm) was collected near Ebensee in Austria (Oberösterreich) at an altitude of 1100 m above sea level. This material has certified the activity of ^{137}Cs , ^{239}Pu , ^{226}Ra , and ^{90}Sr [15].

Certified reference material IAEA 385

A sample of approximately 250 kg of sediment was collected from the Irish Sea (54.3° N, 3.7° W) by the Centre for Environmental, Fisheries and Aquaculture Science (CEFAS), Lowestoft, UK, in 1995. Activities were established for ^{40}K , ^{137}Cs , $^{226,228}\text{Ra}$, $^{230,232}\text{Th}$, $^{234,238}\text{U}$, $^{238, 239+240}\text{Pu}$, ^{241}Am , ^{90}Sr and ^{210}Pb [16].

Sediment leaching

A two-step leaching process will be used to extract and purify meteoric ^{10}Be adhered to the particle surface of the certified reference materials. The procedure was based on that reported by Padilla [17] and Jena [18]. Figure 1 shows a diagram with the outline of the method used. The leaching process results from optimizing the processes presented by Padilla [17] and Jena [18]. In contrast, the radiochemical process has been used in our laboratory based on the analyses presented by Padilla [3].

Aliquot about 1 g was taken in 50 mL centrifuge tubes. First, leaching was carried out in 40 mL acetate buffer at pH=4.66 and placed in an ultrasonic cleaner at 80 °C for 2 h. Then, samples were centrifuged at 4500 r.p.m. for 15 min, and the supernatant was removed. The residue was leaching in a second leaching with 12 mL of Hydroxylamine hydrochloride ($\text{NH}_2\text{OH}\cdot\text{HCl}$) 0.04 M in 25% acetic acid solution and kept for sonication in an ultrasonic at 80 °C for six h to extract the Be from the solid, the sample was centrifuged, and the supernatant was separated for further treatment. 250 μL of standard carrier solution (1000 mg L^{-1} Be for ICP-OES, Certipur Brand) was added to the supernatant and brought to complete

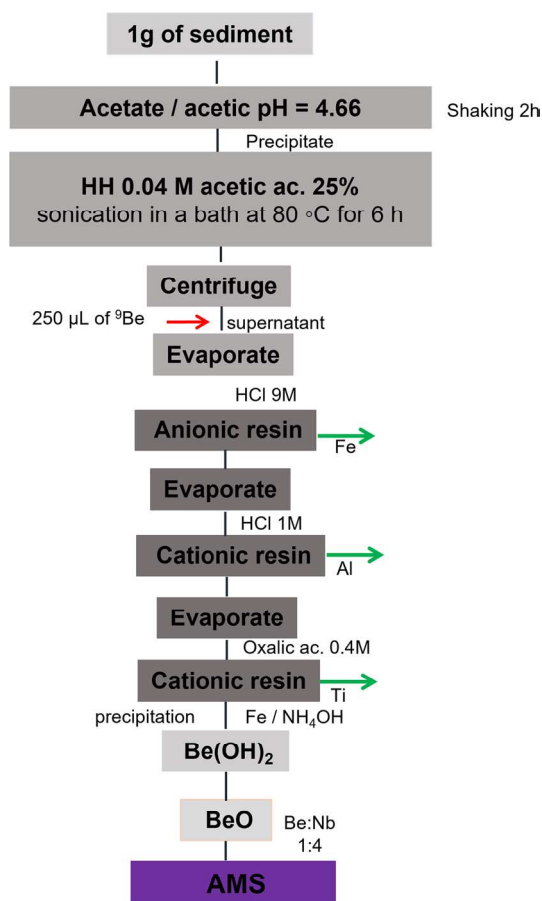


Fig. 1 Scheme for separation and extraction of Be. The leaching of the sample is a mixture of those reported by Padilla [17] and Jena [18]; while the radiochemical extraction process is based on what was established by Padilla [3]

dryness. The residue was re-dissolved two or three times into 10 mL HNO_3 8 M. The remaining sample was dried and recovered with 10 mL HCl 9 M. The dilution obtained from the leaching process was passed through an anion exchange resin (Dowex AG1-X8), where Be was collected with 20 ml of HCl 1 M. This fraction was evaporated and dissolved again in HCl 1 M and poured over a cation exchange resin (Dowex 50W-X8), where Be was eluted using 20 ml of HCl 1 M. Be was precipitated into ammonia and dissolved in a dilution of 0.4 M oxalic acid, which was poured into a cation exchange resin (Dowex 50W-X8), where Be was eluted with 16 ml of HNO_3 0.5 M and 26 ml of HNO_3 1 M. The dilution was evaporated and dissolved in water where Be is precipitated as $\text{Be}(\text{OH})_2$ by adding ammonia at pH=10 [3]. The Be fraction was centrifuged at 4500 r.p.m for ten minutes, eliminating the supernatant. The residue was freeze-dried for 24 h and calcined at 1000 °C. BeO was obtained, mixed with 4 mg of Nb, pressed in aluminum cathodes, and measured by AMS at LEMA, Mexico.

AMS measurement

The samples were measured by the 1 MV AMS system at LEMA [19]. The negative ion beam was produced in a Cs-Sputter ion source on the low energy zone and injected into a magnetic filter, where the BeO^- ions are mass-analyzed and separated. The ions are accelerated in the Tandetron accelerator at 1MV, where the Ar gas is used in the stripping process. Afterward, the beam is analyzed again for mass by a second magnetic filter and energy by an electrostatic analyzer (ESA) on the high-energy zone. Finally, the ions are counted and identified in a two-anode gas ionization detector [20]. The ^{10}B isobar was separated using a silicon nitride degrader foil with thicknesses of 75 nm placed behind the high energy sector magnet [21].

The ^{10}Be measurement was carried out in charge state + 1 after ESA. A complete description of the system tuning is described by De los Ríos [22]. The average currents obtained on the measurements in the high-energy zone were around 1 μA for $^9\text{Be}^+$. A chemical blank was prepared for each block of 8 samples; its preparation was with 250 μL of pure ^9Be following the same chemical process and measured together with the samples. The measured isotopic ratios $^{10}\text{Be}/^9\text{Be}$ were normalized with the 5.1 standard sample, isotopic ratio value $^{10}\text{Be}/^9\text{Be} = 2.7 \times 10^{-11}$ [13]. The normalized isotopic ratios $^{10}\text{Be}/^9\text{Be}$ of blanks were between 2.7×10^{-14} and 3.9×10^{-14} .

Statistical analysis, such as Analysis of Variance (ANOVA), average, standard deviation, minimum, maximum, and coefficient of variation were performed using OriginPro 8.6

Results and discussion

CRMs IAEA-385 and SOIL-6 were characterized for meteoric ^{10}Be concentrations. The results are expressed in the number of atoms g^{-1} dry weight. Each CRM was analyzed in 16 replicates, divided into two batches of 8 samples each, which two analysts processed. Tables 1 and 2 show the statistical data of the ^{10}Be concentration of the eight samples that comprise the CRMs' batches. Figures 2 and 3 show the CRM Soil-6 and IAEA 385 data distribution in the two analyzed batches. The lines represent the individual data of the eight measurements that comprise each batch with their respective standard deviation (points and lines, respectively). At the same time, the box plot shows the distribution of the dataset of each batch.

The mean concentration of the 16 CRM SOIL-6 data was 611 ± 24 million atoms g^{-1} with a variation of 2.1% between data. Batches 1 and 2 of the CRM SOIL-6 show many similarities in the parameters reported in Table 1; they differ in that the uncertainty in batch 2 is lower, but both batches are acceptable, tend to be reproducible and repeatable, and it can be established that the concentration of ^{10}Be in this CRM is 611 ± 24 million atoms g^{-1} with a minimum and maximum value of 591 and 641 millions atoms g^{-1} , respectively.

The ANOVA analysis for the CRM SOIL-6 shows a significance level of $p = 0.05$, and there is no significant difference between the concentration in the two different batches processed by two different analysts ($p = 0.79$). Figure 2 shows schematically the two other groups with their respective data and uncertainties where it can be seen that the concentration values of ^{10}Be meteoric in both batches are very similar, and it is corroborated that the concentration of ^{10}Be meteoric in the SOIL-6 is 611 ± 24 million atoms g^{-1} .

Table 1 Statistical data of ^{10}Be concentration in CRM SOIL-6 ($n = 8$)

	Mean $\pm$ std dev (million atoms g^{-1})	Median (mil- lion atoms g^{-1})	Min (mil- lion atoms g^{-1})	Max (mil- lion atoms g^{-1})	Coef. Var (%)	p value ANOVA
Batch 1	611 ± 24	608	591	641	2.6	0.79
Batch 2	605 ± 17	601	597	619	1.4	

*The data represents the statistics of the 8 samples that comprise each batch

Table 2 Statistical data of ^{10}Be concentration in IAEA-385 CRM ($n = 8$)

	Mean $\pm$ std dev (million atoms g^{-1})	Median (mil- lion atoms g^{-1})	Min (mil- lion atoms g^{-1})	Max (mil- lion atoms g^{-1})	Coef. var (%)	p value ANOVA
Batch 1	101 ± 6	101	97	102	0.71	0.91
Batch 2	101 ± 6	101	99	102	0.62	

*The data represents the statistics of the 8 samples that comprise each batch.

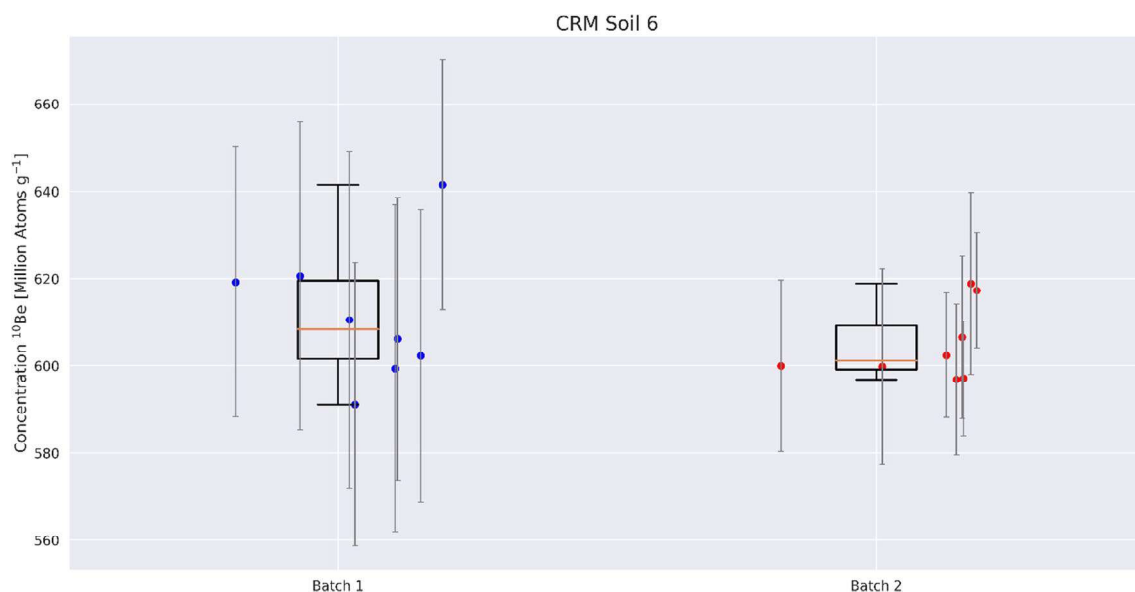


Fig. 2 Meteoric ^{10}Be concentrations in CRM SOIL-6. The box shows where most of the 8 data points in each CRM SOIL-6 batches are concentrated, and the whiskers represent the minimum and maximum values of the range (1.5 times the interquartile range)

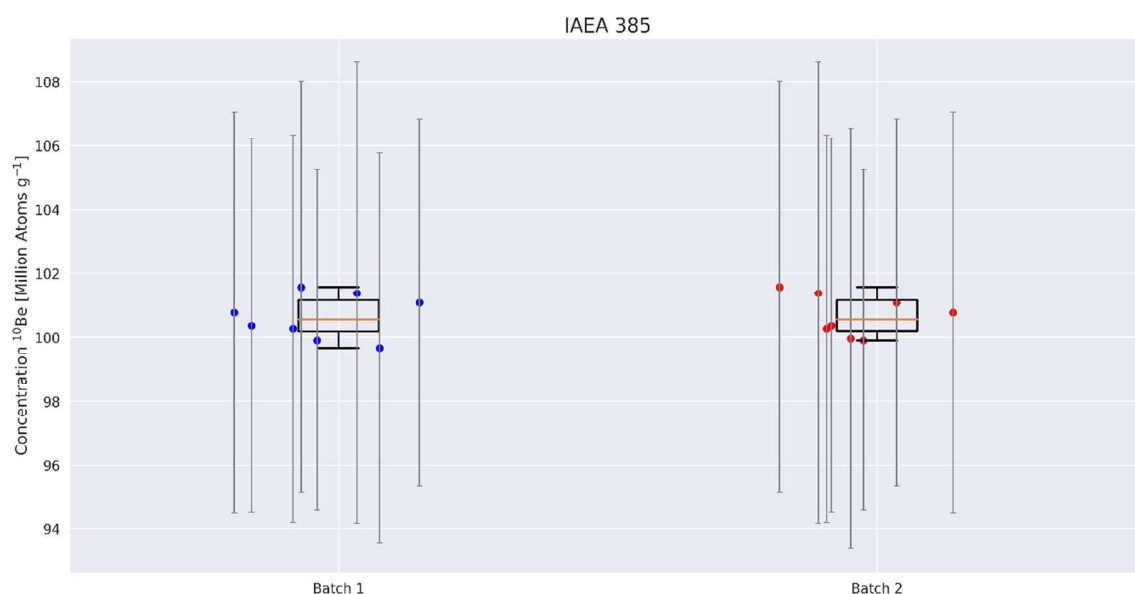


Fig. 3 Meteoric ^{10}Be concentrations in CRM IAEA 385. The box shows where most of the 8 data points in each batch of the CRM IAEA 385 are concentrated, and the whiskers represent the minimum and maximum values of the range (1.5 times the interquartile range)

On the other hand, the mean concentration of the 16 CRM IAEA 385 data was 101 ± 6 million atoms g^{-1} , with a 0.6% variation between the data.

CRM SOIL-6 batches 1 and 2 of the CRM IAEA 385 show significant similarity in the parameters reported in Table 2; even the coefficient of variation in both batches is almost identical, as is the mean meteoric ^{10}Be concentration. The data tend to be reproducible and repeatable, and it can be established that the concentration of ^{10}Be in this

CRM IAEA 385 is 101 ± 6 million atoms g^{-1} with a minimum and maximum value of 97 and 102 million atoms g^{-1} , respectively.

The ANOVA for the CRM IAEA 385, with a $p=0.91$, accepts the null hypothesis and shows no significant difference between the two treatments (batch 1 and batch 2). Figure 3 schematically shows this comparison, where the mean ^{10}Be concentration in both batches is practically the same, with a 101 million atoms g^{-1} value.

The wide repeatability and reproducibility of the data presented suggest that both CRMs analyzed in this research can be used as internal control standards in our laboratory and the entire AMS community for the routine analysis of extraction and measurement of the meteoric ^{10}Be concentration in soil and sediment samples. It should be noted that the ^{10}Be concentrations could depend on the leaching method used, so it is emphasized that the values presented are valid for the methodology described in this work and that it would be necessary to determine the influence of the amount of B present in CRMs.

Conclusions

The measurements of meteoric ^{10}Be concentrations in two CRMs from IAEA were characterized in the IMV AMS system at LEMA. The radiochemical procedure to extract and purify meteoric ^{10}Be was successfully adopted to determine its concentration in soils and sediments. The preliminary results provided in this work are the first ones of meteoric ^{10}Be concentration for these CRMs. The repeatability and reproducibility found suggest that they can be used as internal control standards for the extraction and measurement processes in our laboratory. CRMs SOIL-6 and IAEA-385 have been used for quality assurance and quality control of radionuclide analysis in marine sediments using techniques such as (ICP-MS, TIMS, AMS), specifically, AMS has been used to determine the concentration of Pu radionuclides (^{239}Pu and ^{241}Pu) in IAEA 385. Their potential is also shown in developing and validating analytical methods for determining meteoric ^{10}Be concentration. Comparison exercises with other facilities are suggested to verify the preliminary results obtained in this research and determine the concentration of B after radiochemical separation to establish the impact of B on the BeO prepared for measurement.

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