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Accelerator mass spectrometry (AMS) for beryllium-7 measurements in smallest rainwater samples

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Abstract

Beryllium-7, mainly measured via γ-spectrometry, is used as a (natural) radiotracer for education and science. For activities < 0.1 Bq and samples containing also longer-lived ^{10}Be, accelerator mass spectrometry (AMS) is the method-of-choice. We demonstrate that ^7Be and ^{10}Be can be quantified at the Dresden AMS facility on the same prepared BeO. Detection limits (^7Be) are ~ 0.6 mBq. Samples as small as tens of millilitres of rainwater can be chemically processed (after acidification) within a few hours without expensive and slow ion exchange. Isobar (^7Li) suppression by chemistry and AMS is sufficient to guarantee for an ultrasensitive, cheap, and fast detection method for ^7Be allowing high sample throughput.

Keywords ^7Be · ^{10}Be · Accelerator mass spectrometry · AMS · Rainwater · Atmospheric tracer

Introduction

Beryllium-7 ($T_{1/2} = 53.22 \pm 0.06$ days, [1]) and the longer-lived ^{10}Be ($T_{1/2} = 1.387 \pm 0.012$ Ma, [2]) are produced in similar quantities in the Earth's atmosphere by cosmic-ray-induced spallation reactions, primarily on nitrogen and oxygen [3–6]. The radionuclides are attached to aerosols, transported to the Earth's surface via wet or dry precipitation [e.g. 7], and incorporated into ice/water and attached to grain surfaces in sediments or rock.

Hence, ^7Be alone, in combination with other short-lived radionuclides such as tritium [8, 9] and $^{32,33}P$ [10], or the $^{10}Be/^7Be$ ratio can be used as a time-dependent tracer of various transport processes in the Earth's atmosphere and the environment [3, 11, 12]. Beryllium-7 data can also decipher extraterrestrial processes such as a meteorite's exposure

history [e.g. 13, 14] or variabilities in solar properties such as activity and magnetic field [15, 16].

While the beta-emitter ^{10}Be is routinely and nearly exclusively analysed by accelerator mass spectrometry (AMS) [e.g. 17] after radiochemical separation lasting from a few days [18] to several weeks [19, 20], the gamma-emitter ^7Be is usually determined by its 477.6 keV gamma-line with or without radiochemical separation [21, 22]. AMS has been less frequently applied for ^7Be quantification. Raisbeck and Yiou [11] used AMS as early as 1988 for analysing ^7Be from marine sediments at the now closed French AMS-facility in Gif-sur-Yvette. Nagai et al. [23] performed ^7Be-AMS in Japan (MALT) for sea water and rain and Smith et al. [24] in Australia (ANTARES) for snow pit samples, ice, and rain. More recently, ^7Be-AMS was developed at the Chinese Xi'an AMS facility [25] and the AMS facility at the Lawrence Livermore National Laboratory (CAMS) for a variety of sample matrices [26]. All AMS facilities extract BeO^- from a BeO-AMS-target by Cs-sputtering. Each facility stripped ^7Be and its isobar ^7Li bare of electrons and separated them by charge using an electrostatic analyser. Only Zhao et al. [27] developed an alternative method of separation, on samples of compressed beryllium powder and lithium metal, whereby $^7BeO^{2+}$ was selected and measured in their detector. Since $^7LiO^{2+}$ is unstable, the isobar is suppressed.

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In continuation of our earlier approach to make [7]Be easily accessible world-wide as a radiotracer for educational purposes [28], where we have successfully developed a radiochemical separation for tens-of-litre-samples of rainwater, we also explored the analytical capabilities of the DREsden Accelerator Mass Spectrometry (DREAMS) facility in Germany [17, 29]. To establish [7]Be-AMS at DREAMS, validation measurements by gamma-spectrometry on large rainwater samples were performed at the Institute of Radioecology and Radiation Protection (IRS) in Hannover, Germany [28]. Determination of [7]Be and [10]Be by AMS in the same sample can be also used as a first quality control. Finally, smaller samples containing much lower [7]Be activities were investigated by AMS to demonstrate the full analytical potential.

Experimental

Samples

Two types of rainwater collections were performed on the ground with a minimum distance of 10 m to the next building (see also Table 1):

1. Two large (30 L and 118 L) rainwater samples were collected at the IRS in Hannover (52°23′38.5″N; 9°42′07.8″E). The set-up, used for several sampling campaigns, consisted of a rain collector (1 m^2) and polypropylene boxes, which resulted in a total collection area of 5.36 m^2. For transportation and handling, the rainwater was transferred into 10 L high-density polyethylene (HDPE) storage canisters. No direct acidification in the sampling boxes was performed before transferring the

Table 1 Sample and calibration material details

Sample name	Sample mass (g)	Collection time Time of day (duration)	Collection site	[9]Be addition mass (µg)	Remarks
Hann	117,934	27.02.–10.03.2017	IRS Hannover	4998 ± 25 (commercial; Scharlau)	~45% for AMS (see [28]) divided in 5 AMS-targets (Scharlau: Batch 11863301; 2% HCl, $c($[9]$Be) = (980.4 \pm 4.9)$ µg/g)
Hann May	29,534	18.–19.05.2017	IRS Hannover	2257 ± 11	~48% for AMS; divided in 3 AMS-targets
Drs_05_05	42.55	05.05.2017 (overnight)	HZDR	315.9 ± 1.5	First rain
Drs_05_06	32.63	06.05.2017 (overnight)	HZDR	316.6 ± 1.6	First rain
Drs 0	45.11	12.05.2017 ~ noon	HZDR	315.4 ± 1.5	After heavy rainfall
Drs 1	50.68	03.06.2017 21:00 h (for 15 min)	DRS-Loschwitz	314.7 ± 1.5	~3 h after rain started
Drs 2	18.27	09.06.2017 22:00 h (for 15 min)	DRS-Loschwitz	315.9 ± 1.5	First rain
Drs 3	19.86	16.06.2017 00:30 h (for 15 min)	DRS-Loschwitz	315.2 ± 1.5	First rain
Drs 4	50.37	16.06.2017 00:55 h (for ~ 7 h)	DRS-Loschwitz	316.2 ± 1.5	Not the first 25 min of rain; aliquot from ~ 150 mL in total
Drs 5	48.94	16.06.2017 11:20 h (for 10 min)	HZDR	316.3 ± 1.5	First rain; but it rained the night before
Drs 6	22.24	16.06.2017 12:00 h (for ~ 30 min)	HZDR	310.2 ± 1.5	Not the first 40 min of rain
[7]Be calibration material	0.00736 (Al catcher foil)	May 2017 (p-activation)	Debrecen, HU (p-activation)	3388 ± 17	(350 ± 35) Bq, @ 2.6.2017 11:00 h BeO contaminated with Al_2O_3 ~ 50% of BeO divided in 5 AMS-targets

Except for sample *Hann*, a dedicated low-level (in [10]Be) [9]Be carrier solution was used [30]. *Hann* and *Hann May* samples have been shared (given %) between AMS and counting at Hannover

water of the *Hann* sample (118 L) but it was done for the *Hann May* sample (30 L).

2. Small rainwater samples (18–51 g, see Table 1) were collected in a single 26 cm × 36 cm box (0.09 m²) at HZDR (51°03′44.9″N 13°57′04.5″E) and Dresden-Loschwitz (51°03′02.8″N 13°49′19.7″E), instantly acidified with a few drops of HCl (7.1 M), transferred to a 50 mL syringe and filtered through a polyvinylidenefluoride filter (pore size: 0.45 µm) into a 50 mL centrifuge tube. The collection box was rinsed with very dilute HCl before the next sample collection.

Sample preparation of rainwater samples

For small samples, about 140 µL of a dedicated low-level (in ^{10}Be) ^9Be carrier (2246 ± 11 µg/g) [30] was added to the acidified sample solution (see Table 1). The simplest and fastest chemistry was applied: (a) vortex, (b) addition of ammonia (25%) for $Be(OH)_2$ precipitation, (c) washing one time with 5 mL pH8/9 solution (2 drops NH_{3aq} in 250 mL H_2O) to remove NH_4^+ and Cl^-, (d) wet transfer to quartz crucible, (e) drying, (f) ignition to BeO for 2 h at 900 °C in a muffle furnace, (g) mixing with Nb powder (1:4 by weight), (h) pressing in Cu cathodes, sealed from the back with stainless steel pins. Total preparation time was 6–8 h for a batch of seven to ten samples and total costs are around 15 € per sample.

The chemical preparation of the 118 L sample is described in detail by Querfeld et al. [28]. Prior to transferring from the box, the 30 L sample was acidified to pH 1 with HCl, filtered through 2–4 µm Whatmann™ filter paper, concentrated by a rotary evaporator, and evaporated to dryness by an IR-lamp and a hot plate. The residue was exposed three times to 2.5 mL HNO_3 (69%) and one time to 1.5 mL $HClO_4$ (70%) to destroy any organics. The residue was taken up in ~ 24 g dilute HCl and ^7Be determined by gamma-spectrometry. For inductively coupled plasma optical emission spectrometry (ICP-OES), a small aliquot was sacrificed. The remaining sample (96.8%) was mixed with 2.3 mg of a ^9Be carrier (see Table 1). Further chemical separation of Be from other elements followed the approach of Merchel and Herpers [19] used for meteorites and involved repeated hydroxide precipitation, as well as anion and cation exchange. Final sample preparation was performed similar to the method described for small samples above. Before the final $Be(OH)_2$ precipitation, the sample was divided into three parts.

Preparation of AMS calibration material ($^7Be/^9Be$)

Beryllium-7 as calibration material for quantification of AMS measurements was produced by proton-activation of LiF (natural isotopic composition; evaporated onto a thin catcher foil) at the Tandetron accelerator [31] of the Institute for Nuclear Research, Debrecen, Hungary, using the nuclear astrophysics beamline [32]. The proton energy was 3.030 MeV, the beam current 300 nA for an irradiation time of 10 min.

This technique is well-established and easy to perform if a cyclotron or accelerator is accessible [33]. The desired activity was pre-calculated such that, by the end of sample preparation of several ^7Be-AMS targets, the $^7Be/^9Be$ ratio would be roughly similar (same order of magnitude) but slightly higher than the highest expected sample ratio. This is a common practice in AMS measurements since it greatly reduces the potential for cross-contamination in the ion source (see e.g. [34]).

An Al foil (10 µm thick) was accidentally used as the ^7Be catcher foil instead of the intended, and simpler to chemically separate, Ni (7.5 µm-thick foil). This contaminated the produced BeO with Al_2O_3. The Al foil, containing also the freshly produced ^7Be, was dissolved in 2 mL HCl evaporated to dryness for gamma-counting to accurately quantify the produced ^7Be-activity at HZDR. It was then redissolved in 3 mL HCl (7.1 M), and further treated as small samples described above (but with a 10-times higher amount of a ^9Be-carrier). Only about 50% of this material was finally divided into five AMS targets leaving some material as a back-up.

^7Be gamma-measurements

In complete sample solutions concentrated by evaporation only and representative aliquots (~ 45%) of large rain samples, ^7Be was analysed in a high-purity germanium (HPGe) detector (Ortec: GEM-40200-P; software: Genie2000) [28] at the IRS in Hannover using the characteristic 477.6 keV gamma line [1] (eff: 2% for 1 L Marinelli beaker).

For the calibration material, the dissolved Al foil (2 mL HCl_c) evaporated to dryness, was also analysed by gamma-spectrometry, but instead at HZDR. The evaporated sample of ~ 0.5 cm diameter was situated in a plastic vial atop the detector end cap, centrally in the symmetry axis of the detector resulting in an effective distance of the sample material to the detector end cap of ~ 1.5 cm. The n-type HPGe detector (60% relative efficiency) was placed in a graded shield setup including 15 cm thick lead shielding [35]. The gamma-ray detection efficiency in the measurement geometry was (7.76 ± 0.23)%, determined by a calibrated point-type ^7Be source (earlier measured in far geometry (21.5 cm) using ^{137}Cs and ^{133}Ba activity standards from the Physikalisch-Technische Bundesanstalt (PTB)), which was placed in a plastic vial equal to the one used for the sample. The 477.6 keV peak contained (161,400 ± 400) counts after 20.2 h. By using the half-life of (53.22 ± 0.06) days and a branching ratio of (10.44 ± 0.04) % for the ^7Be decay to the first excited state of ^7Li [1], the number of ^7Be nuclei was

determined to be $(1.84 \pm 0.05) \times 10^9$ (equivalent to 277 Bq), referred to 1 June 2017 12:36 h CEDT.

AMS measurements ([7]Be and [10]Be)

AMS measurements were performed at the 6 MV Tandem accelerator at DREAMS [17, 29]. The AMS targets (BeO) are loaded into a carousel where a piston injects them automatically into the ion source. In the ion source, the sample material is bombarded by Cs^+ ions, sputtered, and a beam of negative BeO^- ions is extracted. The sputtering process is destructive, thus, care must be taken to ensure sufficient material is used for each radioisotope of interest. The negative ion beam reaches the bouncer magnet, which sequentially selects the isotope to be injected into the tandem by mass.

The [10]Be/[9]Be ratios were measured first using *Fast Sequential Injection (FSI)* detailed in [17, 29, 36]. The tandem voltage was chosen so as to maximize the 2+ charge state yield of Be isotopes. Due to the available positions of the offset Faraday cups on the high-energy (HE) side, simultaneously measuring the stable [9]Be (at the Faraday cup) and [7]Be through the reference path, at the fixed terminal voltage, is not possible. To circumvent this, the isotopes were measured using software called *Slow Sequential Injection (SSI)* obtained from High Voltage Engineering Europa B.V. and used e.g. at the AMS facility in Seville, Spain [37].

In SSI mode, [7]BeO^- ions were injected by the low-energy bouncing magnet into the tandem accelerator at a terminal voltage of 4.728 MV. At this voltage, the production of 2+ charge state is dominant (~70%) [38]. The stripped [7]Be^{2+} ions were bent by the HE-magnet down the reference path and stripped to the 4+ charge state by a 3.1 µg/cm^2 silicon nitride foil. At constant mass of 7 amu, the charge state of 4+ is selected using the electrostatic analyser (ESA) in order to suppress the isobar and decay product of [7]Be, [7]Li, since the charge state of 4+ does not exist for [7]Li.

For the measurement of [9]Be, the bouncer magnet voltage was changed to allow [9]BeO^- into the tandem accelerator, which was set to terminal voltage of 3.2 MV leading to a charge state yield of ~68% for [9]Be^{2+}. The tandem voltage was changed to allow the bending of the [9]Be^{2+} into the movable Faraday cup following the HE-magnet while keeping the magnetic field fixed.

Each SSI sequence involved the injection of [7]BeO^- ([7]$Be^{16}O^-$) for 40 s and [9]BeO^- ([9]$Be^{16}O^-$) for 2 s. Unfortunately, due to a timing flaw in the setup of the measurement, the bouncer and tandem voltages were changed in such a way that they briefly scattered high currents of particles from the tandem into the gas ionization chamber (GIC) at each transition. As a quick fix to preserve the foils and the GIC itself, two additional steps (2 s each) were set up to offset the changing of the bouncer voltage from the changing of the terminal voltage.

Finally, the software added a default pause of 5 s between each step. Thus, the steps of a single sequence follow: 2 s [9]Be, 5 s pause, 2 s "dummy1", 5 s pause, 40 s [7]Be, 5 s pause, 2 s "dummy2", 5 s pause.

With this approach, the cathode was being sputtered, consuming the BeO material, for 36% of the time with no data recorded. In the end, the radioisotope of interest reaches the GIC as [7]Be^{4+} and is counted atom by atom.

We are aware that in general the SSI mode is inferior to the FSI mode with respect to data precision. The SSI mode is susceptible to larger uncertainties resulting from potential drifts in the Be current resulting from variations in ion output from the sample itself and transmission through the machine set-up. However, this uncertainty is yet outweighed by the one from counting statistics.

In small samples and aliquots of large samples (~40%), [7]Be and [10]Be were quantified versus the aforementioned [7]Be calibration material and the in-house [10]Be standard SMD-Be-12 [17], where the latter is traceable to NIST4325 [39].

AMS measurement of [7]Li to test chemical and AMS isobar suppression

Because we reduced the chemical sample separation to a minimum for all small volume samples and also for the calibration material (containing macroscopic amounts of LiF), we wished to ensure that the isobar [7]Li was sufficiently depleted. To compare [7]Li concentrations in BeO prepared from all sample materials we allowed both [7]Li^{3+} and [7]Be^{3+} into the GIC to separate them via their difference in stopping power. At the same time, we checked whether separation of [7]Li in the GIC is already sufficient or whether full separation of [7]Li from [7]Be using additional stripping to the 4+ charge state is required. As for the case described above, 7 amu and 2+ charge state ions from the accelerator were bent into the reference path by the HE-magnet. Both passed through the degrader foil acquiring a distribution of charge states. The ESA and final 30° magnet were tuned to accept the expected energy of [7]Li^{3+} into the GIC. Each of these steps were performed with most of the apertures in—transmitting only near-axis components—to reduce the abundant Li signal. A few BeO samples from each sample type (some small Dresden and both large Hannover rainwater samples), as well as the LiF calibration material (Table 1), some BeO blanks, and graphite pressed in Al and Cu sample holders, were studied in this manner.

Results and discussion

Chemical and AMS separation of the isobar [7]Li

The results of the relative isobaric abundances in BeO from various samples (small and large rainwater samples, LiF

calibration material, blanks) together with graphite pressed in Al and Cu, respectively, are presented in Fig. 1.

The objectives of these investigations were: (1) proving whether or not ^{7}Be can be separated from its isobar ^{7}Li in the detector, and (2) to test the rapid chemical separation protocol for its performance.

Firstly, we found that separation by stopping power in the gas ionization detector was clearly inferior to separation by charge state since the ion beam had to be severely attenuated (with most apertures in) to be at a level where the ^{7}Li could be introduced into the detector without damaging it. Since separation by charge states was proven and superior with respect to source-to-detector efficiency, there was no further investigation on this modality.
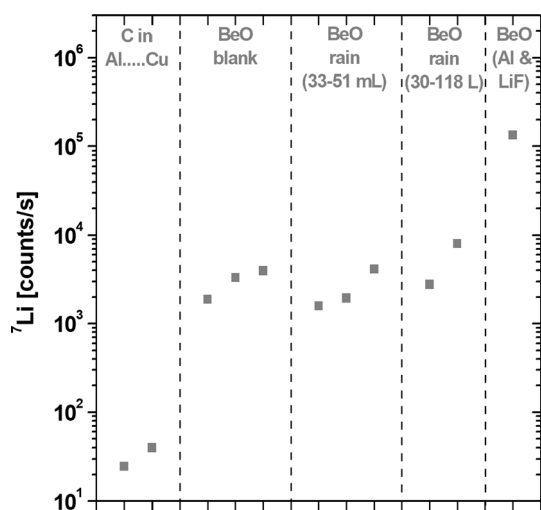

Fig. 1 Relative abundance of ^{7}Li in BeO from different materials, carbon pressed in Al and Cu, respectively, and BeO blanks

Secondly, the small volume samples and the blanks processed with fast and cheap chemical processing had roughly the same amount of ^{7}Li as the larger samples that were treated with more lengthy procedures. Thus, for the purpose of reducing the concentration of the isobar present in each target to a level not harming the silicon nitride foil, the simple chemistry on small samples is sufficient.

AMS results (^{7}Be and ^{10}Be) for small and large rainwater samples

The AMS results are presented in Table 2 and Figs. 2 and 3. All ^{7}Be data was corrected to the collection time. The ^{7}Be/^{9}Be ratios are more a confirmation of sample preparation procedure than a meaningful result since their value depends mostly on the volume of sample collected and the amount of ^{9}Be carrier added. The ^{7}Be/^{9}Be ratios confirm that the activity of the reference material was well-prepared to suit the purpose having similar (slightly higher) ratios for calibration materials than samples to be analysed.

The isotopic ratios of the AMS measurements and the activities provided by the gamma-counting measurements were converted to ^{7}Be atoms g^{-1} at the respective collection times. *Hann* was measured to be $(4.14 \pm 0.17) \times 10^3$ atoms g^{-1} and $(4.37 \pm 0.23) \times 10^3$ atoms g^{-1} and *Hann May* was measured to be $(24.68 \pm 0.95) \times 10^3$ atoms g^{-1} and $(23.44 \pm 0.76) \times 10^3$ atoms g^{-1} by gamma-counting and AMS, respectively. Thus, the AMS results are in excellent agreement with the gamma-counting validation measurements.

Figure 2 shows both the concentrations of ^{7}Be and ^{10}Be in atoms per gram of rainwater. The ^{7}Be values varied relatively little for all of the samples that were collected late in a rainfall; e.g. 8–10% deviation from their mean ^{7}Be

Table 2 AMS isotopic ratios and ^{7}Be concentration at time of collection

Sample name	^{7}Be/^{9}Be [10^{-14}][b]	^{10}Be/^{9}Be [10^{-14}][b]	^{10}Be/^{7}Be	^{7}Be [10^3 atoms g^{-1}]	^{10}Be [10^3 atoms g^{-1}]
Hann[a]	154.2 ± 8.1	$14{,}171 \pm 273$	91.9 ± 5.1	4.37 ± 0.23	401.3 ± 7.7
Hann May[a]	459 ± 15	6228 ± 334	13.57 ± 0.85	23.44 ± 0.76	318.0 ± 1.7
Drs 05_05	15.4 ± 2.0	18.3 ± 1.7	1.19 ± 0.19	76 ± 10	90.7 ± 8.6
Drs 05_06	22.6 ± 2.9	35.1 ± 2.4	1.55 ± 0.22	147 ± 19	227 ± 15
Drs 0	6.69 ± 0.43	11.7 ± 1.1	1.75 ± 0.20	31.2 ± 2.0	54.7 ± 6.2
Drs 1	7.36 ± 0.44	9.7 ± 1.2	1.32 ± 0.18	30.5 ± 1.8	40.4 ± 5.5
Drs 2	6.34 ± 0.40	9.8 ± 1.1	1.55 ± 0.19	73.2 ± 4.7	113 ± 14
Drs 3	7.09 ± 0.43	13.6 ± 1.1	1.92 ± 0.20	75.2 ± 4.6	145 ± 15
Drs 4	8.77 ± 0.42	14.0 ± 1.1	1.59 ± 0.15	36.8 ± 1.8	58.6 ± 5.6
Drs 5	5.8 ± 1.3	8.7 ± 1.7	1.50 ± 0.43	25.1 ± 5.5	38 ± 11
Drs 6	4.03 ± 0.29	10.0 ± 1.0	2.49 ± 0.30	37.5 ± 2.7	93 ± 11
^{7}Be calibration mat.	811 ± 20				

[a]Both Hannover samples contain excess ^{10}Be and are depleted in ^{7}Be

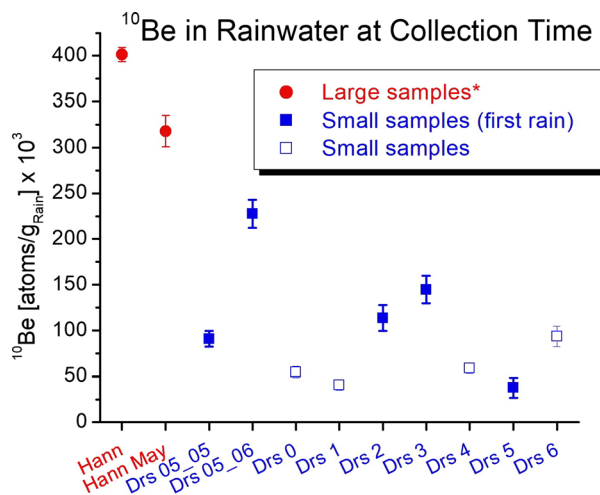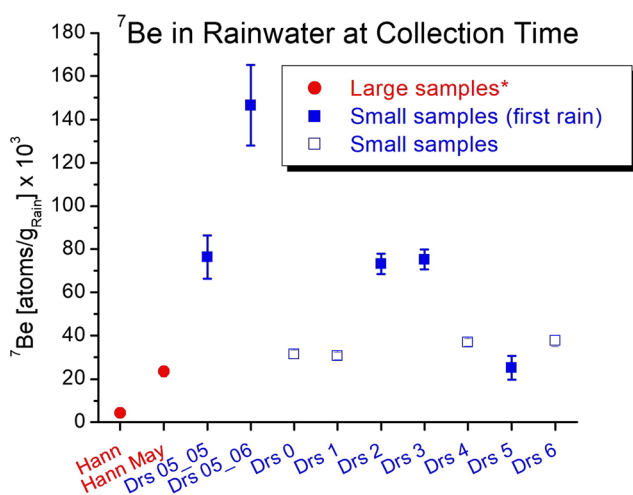[b]The given ^{7}Be/^{9}Be and ^{10}Be/^{9}Be are mainly a function of sample size and ^{9}Be carrier addition

Fig. 2 Concentrations of [7]Be (left) and [10]Be (right) of rainwater water samples. Note samples *Drs 05_05, Drs 05_06, Drs 2,* and *Drs 3* were collected at the start of rainfall containing a larger amount of dust.

Drs 5 was also collected at the start of its rainfall but it had rained the night before, likely depleting the air of particulate matter. *Both Hannover samples contain excess [10]Be and are depleted in [7]Be
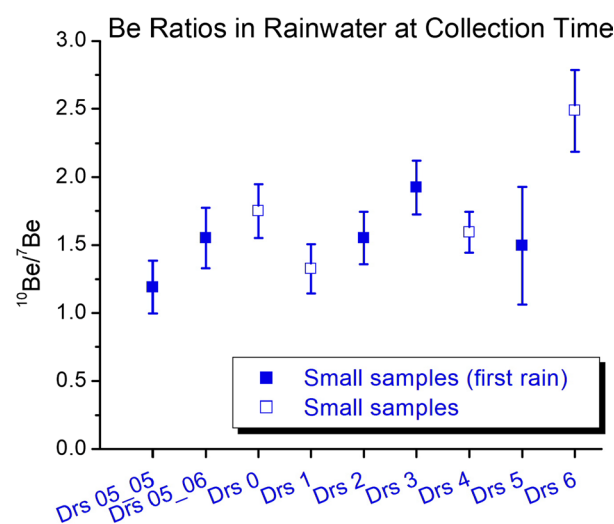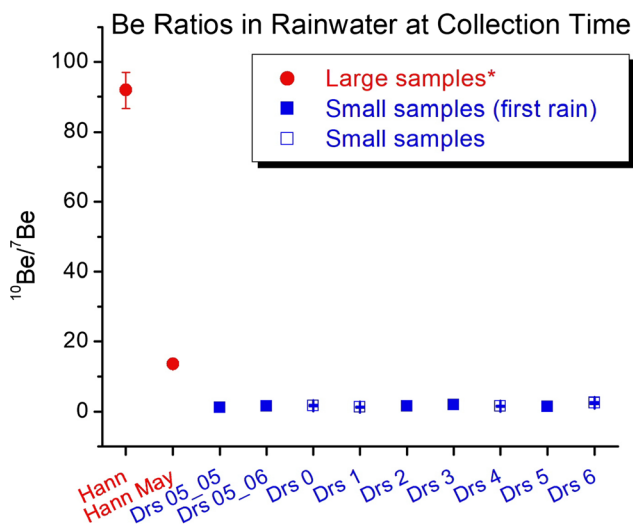

Fig. 3 [10]Be/[7]Be isotope ratios of all rainwater samples (left) and of small samples from Dresden only (right). *Both Hannover samples contain excess [10]Be, and *Hann* was also depleted in [7]Be

value for *Drs 0, Drs 1, Drs 4, Drs 6*. However, five samples (*Drs 05_05, Drs 05_06, Drs 2, Drs 3, Drs 5*) were all collected at the very beginning of their respective rainfall and, with the exception of *Drs 5*, show an elevated amount of [7]Be and [10]Be. This effect is more prominently seen in the [7]Be, which would result almost exclusively from "recent" atmospheric production whereas some [10]Be may be present as old, re-suspended dust causing an elevated background level of [10]Be. Both radionuclides suggest scavenging and enrichment in dust for rain collected at the beginning of a rainfall. *Drs 5* does not follow this trend, likely because it had rained the previous night, which washed out most of the dust in the air before this rainfall collection.

Beryllium attaches to (container) surfaces at pH levels ≥ 5. Because the Hannover sample containers were used for repeated rain collections without the (crucial) acidification, the consequences for the *Hann* samples were: (1) Some Be remaining in the boxes, i.e. non-quantitative transfer, resulting in [10]Be and [7]Be concentrations that were too low (but correct [10]Be/[7]Be), and (2) Short-lived [7]Be decaying in the boxes while waiting for the next rain sample (up to several weeks, see collection time in Table 1). The [7]Be-depleted Be will be partially leached from the boxes for the next sample. This results in too low [7]Be relative to [10]Be, i.e. too high [10]Be/[7]Be. It has to be mentioned that sample *Hann* was collected in several portions (also in many boxes, each

of them having absorbed Be), thus, the first consequence adds for *Hann.* The second consequence affects both, the *Hann* sample and the next sample, *Hann May*. Both Hannover samples contain excess ^{10}Be and *Hann* was additionally depleted in ^{7}Be (Table 2).

An important lesson to be learned from these observations is that acidification (pH < 5) of the rainwater before transfer is highly recommended in order to overcome the above mentioned consequences. In addition, cleaning of the sampling containers with slightly acidic water after each sampling campaign is crucial. Beryllium will also be adsorbed on dust and organic matter (e.g. leaves, pollen, insects) in the sample, thus, acidification before any filtration is extremely important. Since the sampling boxes had not been cleaned with acidic water before both *Hann* and *Hann May* were collected, and the acidification for *Hann* was also omitted before filtration, the ^{7}Be and ^{10}Be values of both were found to be unreliable for the purpose of this study and cannot be used for further interpretation. It should be noted, though, that the original intention of the initial project, detailed in Querfeld et al. [28], was to collect ^{7}Be only. Thus, no attention had been paid to remove residual ^{10}Be or ^{7}Be-depleted Be between (fractions of the *Hann*) samples. Cleaning steps to remove previous beryllium from the sample collection container used in Dresden were performed as the study goal developed further.

The ^{10}Be/^{7}Be ratios (Table 2; Fig. 3) of rainwater samples collected in Dresden are in agreement with each other, range from 1.2 to 2.5, and are consistent with values presented by other labs. For rainwater samples, others report ^{10}Be/^{7}Be ranges of 1.5–2.9 [11], 1.4–2.9 [12], 1.3 [25], and 1.7–4.1 [26]. In air filter samples, Zanis et al. [40] and Yamagata et al. [41] report ranges of 1.5–2.7 and 1–2, respectively. The effects of the previously discussed deviations in the collection procedure in Hannover are obvious in this plot and illustrate the importance of acidifying the rainwater to prevent adhesion to the collector walls as well as rinsing the collectors with acidified water between sampling campaigns for accurate ^{7}Be and ^{10}Be concentrations and ^{10}Be/^{7}Be ratios.

Potential for lower ^{7}Be AMS uncertainties and lower detection limits

The total uncertainty of ^{7}Be AMS data of all rain samples is 6–7% with the exception of *Drs 5* being at 22%. In contrast to all other samples (chemical yield for BeO ≥ 94%), the chemical yield for BeO for *Drs 5* was inexplicably very low (21%), hence, it produced low ion currents and was quickly consumed. *Drs 05_05* and *Drs 05_06* were measured for a short time during the first feasibility test runs yielding higher uncertainties. Due to insufficiently low count rates in a later beam time, they were not re-measured. In all cases, the uncertainties were dominated by counting statistics. An

improvement in the switching time of the *SSI-mode* measurements can only improve this. We are working with the developers of the proprietary *SSI-mode* software to eliminate the need for the aforementioned "dummy" steps. This as well as optimizing all other switching times will maximize the amount of counting time, and therefore number of counts detected on a given sample, reducing the relative uncertainty. The 3% uncertainty of the measurement of the calibration material by decay counting (for 0.8 day) provided an additional but small systematic contribution. If necessary, it is expected that this can be reduced to 1% by measuring longer and in an underground facility [42]. The counting background, mainly due to cosmic ray-induced effects, can in principle be further suppressed by two or three orders of magnitude, using e.g. the new HZDR underground facility *Felsenkeller* [43]. Last but not least, reducing the time between sample collections, chemical processing, and AMS measurements will also improve statistics as more short-lived ^{7}Be has not yet decayed and is still available for the actual measurement.

Our detection efficiency for ^{7}Be (including the negative ion yield) from the target to the detector is 2.4×10^{-4}. Our blank value for ^{7}Be/^{9}Be (5×10^{-16}) is comparable to AMS blank values elsewhere [e.g. 23, 24, 26]. Decay counting has been reported for ^{7}Be samples with activities as low as 25 mBq [44], however such low activities require counting times of many days (e.g. 16 days). For activities lower than this, a considerable amount of time must be invested to measure with reasonable levels of uncertainty [23]. A detection limit of ~ 7 mBq can be reached within unreasonable counting times of 100 days at the *Felsenkeller* [43]. A value of about 60 mBq, enriched by filters collecting for 24 h air volumes of 500–1000 m^3/h, is documented from investigations of ^{7}Be concentrations in air as measured by the CTBTO (Comprehensive Nuclear-Test-Ban Treaty Organisation) global monitoring system [45]. Our AMS measurements push this threshold to 0.6 mBq, which is at least one-to-two orders of magnitude more sensitive and requires only very simple and fast chemical preparation as well as much smaller samples. The efficiency can improve by removing the aforementioned "dummy" steps and by optimizing the tuning/machine setup (could improve by a factor of three), which is also expected to reduce our uncertainty.

Conclusions and outlook

Measurements of ^{7}Be and ^{10}Be have proven feasible at DREAMS on the same BeO prepared from rainwater samples. Simple, cheap, and fast chemistry to prepare BeO-AMS targets from small rainwater samples worked very well when special attention was paid to acidifying rainwater before transfer from collection boxes and filtration takes place. The

overall costs (human resources and chemical products) and speed for chemical separation had been reduced making ^{7}Be-AMS very compatible to e.g. counting techniques (without or including radiochemical enrichment) for routine analyses. Especially, for projects with high sample through-put AMS can be superior over long-lasting counting.

Total uncertainties of sample measurements were usually 6–7%. Validation measurements by gamma-counting of the two large rainwater samples were in excellent agreement with our AMS results. The detection limit for ^{7}Be measurement at DREAMS is 0.6 mBq, which is one-to-two orders of magnitude better than "standard/ordinary" and "sophisticated" decay counting (e.g. in an underground laboratory). Both the limit and uncertainty can be improved by more precise decay counting measurements of the calibration material, the removal of so-called "dummy" steps currently required by the switching software, and better tuning conditions.

Our ^{7}Be and ^{10}Be data showed that the very first rain (< 5 min) collected was enriched in particulate matter. Thus, AMS optimised for small samples has the potential for time evolution studies of rain using ^{7}Be and ^{10}Be as a natural tracer. Additionally, the low detection limit and the high sample throughput will enable future studies where high-precision measurements of small timescale phenomena, thus, small sample volumes are of interest.

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