Chmeleff, J., von Blanckenburg, F., Kossert, K., Jakob, D. (2010): Determination of the 10Be half-life by multicollector ICP-MS and liquid scintillation counting. - Nuclear Instruments and Methods in Physics Research / B, 263, 2, 192-199

DOI: 10.1016/j.nimb.2009.09.012

Determination of the ^{10}Be half-life by multicollector ICP-MS and liquid scintillation counting

Nuclear Instruments and Methods in Physics Research Section B: Beam Interactions with Materials and Atoms (2009) doi:10.1016/j.nimb.2009.09.012

Jérôme Chmeleff[1,4], Friedhelm von Blanckenburg[1,5], Karsten Kossert[2], and Dieter Jakob[3]

[1] Institut für Mineralogie, Leibniz Universität Hannover, Callinstr. 3, D-30167 Hannover, Germany
[2] Physikalisch-Technische Bundesanstalt, Bundesallee 100, D-38116 Braunschweig, Germany
[3] Zentrum für Strahlenschutz und Radioökologie, Leibniz Universität Hannover Herrenhäuser Str. 2, D-30419, Hannover, Germany.
[4] Present address: Laboratoire de Mécanique et Transfert en Géologie, UMR 5563, 14 avenue Edouard Belin, 31400 Toulouse, France.
[5] Present address: German Research Centre for Geosciences GFZ, Telegrafenberg, 14473 Potsdam, Germany

Corresponding author:chmeleff@lmtg.obs-mip.fr

Abstract

A new method was designed and used for determining the half-life of the isotope ^{10}Be. The method is based on (1) accurate ^{10}Be/^{9}Be measurements of ^{9}Be-spiked solutions of a ^{10}Be-rich master solution using multicollector ICP mass spectrometry (MC-ICP-MS) and (2) liquid scintillation counting (LSC) using the CIEMAT/NIST method for determining the activity concentrations of the solutions whose ^{10}Be concentrations were determined by mass spectrometry. Important requirements for the success of this approach a) was the previous coating of glass ampoules filled for counting experiments with ^{9}Be, thereby reducing the risk of the adsorptive loss of ^{10}Be; b) the removal of Boron from solutions to be measured by MC-ICP-MS by cation chromatography without the introduction of mass fractionation and c) the accurate determination of the mass bias of ^{10}Be/^{9}Be measurements by ICP-MS which are always affected by the space-charge effect. The mass bias factor was determined to be 1.1862 ± 0.071 for ^{10}Be/^{9}Be from careful fitting and error propagation of ratios of measured Li, B, Si, Cr, Fe, Cu, Sr, Nd, Hf, and Tl standard solutions of known composition under the same measurement conditions. Employing this factor, an absolute ^{10}Be/^{9}Be ratio of 1.464 ± 0.014 was determined for a first dilution of the ^{10}Be-rich master solution. This solution is now available as an absolute Be ratio standard in AMS measurements. Finally, a half-life of (1.386 ± 0.016) My (standard uncertainty) was calculated. This value is much more precise than previous estimates and was derived from a fully independent set of experiments. In a parallel, fully independent study using the same master solution, [35] have determined a half life of (1.388 ± 0.018) My. The combined half life and uncertainty amounts to (1.387 ± 0.012) My. We suggest the use of this value in nuclear studies and in studies that make use of cosmogenic ^{10}Be in environmental and geologic samples.

1. Introduction

Over the past decades, the number of studies using the rare cosmogenic nuclide ^{10}Be in the geologic, oceanographic, and climate sciences has increased dramatically. This nuclide has thus become one of the most frequently measured cosmogenic isotopes using an Accelerator Mass Spectrometer (AMS). Yet no consensus exists on a reliable value for the half-life of

^{10}Be. Several determinations of this half-life have been done in the past (Table 1, and see also [12], for a review), leaving a discrepancy of 14% between different estimates and splitting the community of users. Although these discrepancies did not compromise exposure ages and erosion rate determinations using in-situ produced ^{10}Be, as long as the half-life used for production rate determinations and unknown samples are the same, the lack of a reliable half-life becomes an issue when dealing with exposure ages for old samples or ages (see [12] for a review), determining burial ages based on the decay of the ^{26}Al/^{10}Be ratio, or if marine sediments and Fe-Mn crust growth rates are to be dated. Therefore, there is a requirement for an accurate and precise value for the ^{10}Be half-life. Moreover the AMS measurements also depend on this half-life because measured ^{10}Be/^{9}Be ratios are always reported relative to AMS standards that were calibrated using a decay constant (see [10] for a complete review).

The requirements for a determination of the ^{10}Be half-life are a solution with known ^{10}Be concentration (with high precision, usually measured with isotope dilution mass spectrometry) and a precise measurement of the activity concentration (activity divided by mass of solution) of that solution. The cause for the deviating estimates reported above potentially arise from discrepancies in the ^{10}Be activity measurements or errors in the dilution series prepared [13,10]. Most importantly, however, they arise from the inability of any mass spectrometric technique used in these studies to measure accurate ^{10}Be/^{9}Be ratios. This is because all methods used so far (AMS, RIMS, SIMS) are affected by an unknown mass discrimination. To circumvent this problem, Nishiizumi et al. [10] have performed an implantation experiment from which absolute ratios of commonly used ICN and NIST AMS standards were measured. Yet the half-life they calculated from those concentration measurements is based on the activity originally measured in the old ICN solution and might be subject to the mentioned systematic errors in the dilution series.

The technique we present here is innovative and totally independent of previous studies. The method is based on measurements of ^{10}Be/^{9}Be isotope ratios by multicollector ICP Mass Spectrometry, the derivation of ^{10}Be concentrations (via isotope dilution using a gravimetrically prepared ^{9}Be spike) from several dilutions, and on accurate activity measurements by means of liquid scintillation counting (LSC).

2. Methods and analytical techniques

2.1 Source and preparation of the starting solution (dil1)

A concentrated solution (approximately 47.5 µg Be in 0.54 g of solution) with a high ^{10}Be/^{9}Be ratio (of the order of 1.4) was obtained from TU München [35]. This solution is sufficiently rich in ^{10}Be to allow for measurement with MC-ICP-MS and will be referred to as the master solution. The concentrated master solution arrived in a quartz ampoule. From this ampoule, a 20 mL starting solution was produced by adding ultrapure HNO_3 and called dil1. Before this dilution process, the master solution was stripped of its boron (see section 2.4.1 for an explanation of the importance of this step). The method used a 1 mL cation exchange column derived from [14,15] but used HNO_3 instead of HCl as exchange medium on the cation exchange column. Light isotopes are known to fractionate on ion exchange columns [16] (and more specifically [17] for Fe, or [18] for Li). Therefore we performed a test of the potential isotope fractionation of Be during cation exchange. We performed isotope ratio measurements of aliquots of the eluates of both column methods (HNO_3 and HCl) using dil1 as a bracketing standard. The measured ^{10}Be/^{9}Be ratios agree within the achieved measurement uncertainty obtained with MC-ICP-MS (Fig. 1). This demonstrates that the separation chemistry with HNO_3 as exchange medium does not fractionate the ^{10}Be/^{9}Be ratio more than the achieved precision of about 0.5%. The same result was obtained with HCl.

2.2 Production of a ^{9}Be spike

A ^{9}Be solution was prepared by dissolving a precisely weighed amount of metallic Be flakes (with a minimum purity of 99.5% purity from Mateck). The ratio ^{10}Be/^{9}Be from commonly used commercial ^{9}Be carriers is typically 2×10^{-14} and thus the ^{10}Be contribution of that solution can be neglected in the final calculations. The Be concentration was measured and controlled several times by multiple ICP-OES measurements (24 total during different sessions) against international (NIST-SRM951) and in-house standards using different dilutions and wavelengths. The relative uncertainty in the concentration of this solution is found to be 0.8% from the combination of all weighing uncertainties. The ^{9}Be concentration of this spike used for calculations is then $(1.359\pm0.011)\cdot10^{16}$ atoms·g^{-1} .

2.3 Dilution series

The starting solution (dil1) has been diluted to different degrees with 1M HNO_3 (dil2 to dil4) to create different solutions with the same ^{10}Be/^{9}Be ratio. The HNO_3 (15M) used to prepare these dilutions was ultrapure and double-distilled, stored in Teflon bottles (to avoid any B contamination), and was used for all dilutions, purification steps and ICP measurements. The purpose of these different degrees of dilution was to allow MC-ICP-MS measurements at different ion beam intensities and using different collector set-ups (Tables 2 and 3). This diversity in collector settings allowed a test of accuracy and improved the overall precision on the ^{10}Be/^{9}Be ratio of the dil1. Three of those dilutions have also been spiked with different amounts of the ^{9}Be spike derived from the dissolution of the metal.

2.4 Multicollector ICP-MS

In order to run samples at sufficiently high signal intensity, the mass spectrometer (ThermoFinnigan Neptune MC-ICP-MS described in [19]) was operated in low-mass resolution mode. Gas flows and ion optics were optimised on a daily basis in order to achieve the highest sensitivity and signal stability as well as the best peak shape for ^{9}Be. The operating parameters used are summarized in Table 4. The stability and flatness of the isotopes' plateaus were checked prior to the measurements. Faraday amplifiers ($R=10^{11}\Omega$) as well as the Secondary Electron Multiplier (SEM), operated in ion counting mode, were used as detectors. Gain factors were calibrated and electronic baselines were determined before each measurement session. Typical ion beam intensities for each set-up as well as typical analyte background counts can be found in Table 3. A cyclonic spray chamber made of PEEK (AHF), a microflow nebulizer (made of PFA), and a sapphire torch were used instead of a normal glass system to allow for cleaning by HF and to reduce B levels.

Several dilutions of the first solution were measured with different signal intensities. Thus, three types of measurements were used: F: all isotopes were detected by Faraday collectors; S: all isotopes detected by the SEM; SF: a combination of Faraday and SEM (Table 2). ^{11}B had to be monitored during ^{10}Be/^{9}Be measurements (see section 2.4.1 on ^{10}B correction), and thus a dynamic mode was employed both for Faraday and SEM measurements. Different integration times have also been used (Table 2). Every measurement consisted of 20 cycles at 2 or 4 seconds each. Samples were presented in 1M HNO_3. Between measurements, a washout time of 3 min was kept in which a 1M HNO_3 solution was flushed through the uptake system. Procedure blanks (representing all steps of chemical sample processing) contained the same amounts of ^{9}Be, ^{10}Be + ^{10}B, and ^{11}B as the wash solution ("on-peak zero") (Table 3). Thus, the on-peak zero measurement was representative of a combined B and Be blank correction. The on-peak zero was measured every 5 measurements. The average of the previous and consecutive on-peak zero measurement was subtracted from the 5 sample analyses measured in-between.

Possible spectroscopic interferences during ^{10}Be/^{9}Be measurements can mostly be found on the mass 10 which, in addition to ^{10}Be, is ^{10}B and ^{9}BeH. No evidence of ^{9}BeH interference on ^{10}Be has been found with a pure solution of ^{9}Be measured under normal conditions as well as a high mass resolution (resolving power, as defined in [19], m/dm=10000). The ^{10}B contribution cannot be resolved from ^{10}Be with this MC-ICP-MS system, as the resolving power needed would be approximately 17000, and thus it has been monitored and corrected for, as explained in the following part.

2.4.1 *^{10}B correction with ^{11}B monitoring*

To measure ^{10}Be without ^{10}B interference, care had to be taken to 1) ensure a sample solution in which the boron levels were as low as possible and 2) to control the possible interference of ^{10}B and to correct for it. The first point has been taken care of by using Be purification chemistry (derived from [14,15], see 2.1) that includes a B/Be separation. Concerning the second point, ^{11}B had been monitored during each measurement (Table 2). The ^{10}B contribution was then subtracted from the measured total mass 10 signal (representing ^{10}Be+^{10}B) using the ^{11}B/^{10}B of the procedure blank solutions.

2.4.2 Determining the mass bias factor correction

When using MC-ICP-MS, the isotope ratio of any element measured is different from the true isotope ratio. If all parameters are kept identical between measurements (position of the torch, acid strength of solutions, sample and skimmer cones, spray chamber and torch), the so-called mass bias is mainly controlled by the so-called space charge effect [20,21,22]. The plasma in an ICP source is a positively ionised gas where particles repulse each other and light isotopes move into the outer region of the plasma. Since the region of the plasma sampled into the mass spectrometer is small and also in the centre of the plasma, heavy isotopes are extracted preferentially and the actual measured ratio of a heavy mass divided by a light mass is always higher than that of the aspired solution. This effect is usually controlled via the “standard/sample bracketing technique” or, alternatively, “doping” with another element, assuming the mass bias of the standard or doping element is identical to that of the sample [23,24]. None of these techniques could be used for Be – first, because no ^{10}Be/^{9}Be standard exists for MC-ICP-MS and, second, because the closest elements to Be (Li and B) differ in their mass bias (Table 5). The mass bias is usually corrected using a power law or exponential law [25,23]. We used the power law calculated from the fit in Fig 2 from a wide range of different elements (Li, B, Si, Cr, Fe, Cu, Sr, Nd, Hf, Tl, U), measured with the same sampling system as that used here, to decipher the mass bias for Be. Li and B, which are direct neighbours of Be in their mass, have both been measured under all possible conditions encountered during Be measurements (spray chamber, gas flows, torch position) to provide an estimate for the maximum possible variation in mass bias. Note that these measurements also included a switch from an instrument in Hannover to one in Zurich (Fig 3).

To evaluate the uncertainty of this estimate of the Be mass bias factor, we performed a Monte Carlo simulation using the uncertainties of the different mass bias factors to simulate one thousand power law fits through the data. The exponential law has been tested as well and gave a final result identical within uncertainty, power has then be chosen for convenience of representation of a great number of curves. Figure 2 shows the average curve as well as the two extreme curves that give the global shape of all calculated and fitted curves (in Fig. 2b). The extreme curves were used to calculate the uncertainty on the mass bias correction factor. Those extreme curves give a very conservative estimation of the uncertainty (representing the total possible variation of the mass discrimination factor). Note that there is a small asymmetry between the higher and lower curve, we chose to only take the higher uncertainty and make it symmetrical as the difference wasn't recognizable in the final number. This simulation was then used to calculate the average mass bias factor and the associated standard uncertainty. The resulting mass bias correction factor for ^{10}Be/^{9}Be is then 1.1862 ± 0.0071.

2.5 Activity measurements by means of liquid scintillation counting

Weighed aliquots of the ^{10}Be solutions (dil1 and dil2) were transferred into PTB-type glass ampoules which have been pre-treated with inactive carrier solution (90 µg $BeCl_2$ in 1 g of HCl with a concentration of 0.1 mol/L) to reduce adsorption effects on the glass walls. The ampoules were then flame-sealed and sent to PTB for activity measurements by means of liquid scintillation counting. The samples for liquid scintillation counting were prepared with 15 mL Ultima Gold^{TM} AB scintillator in 20 mL low-potassium borosilicate glass vials. Small amounts of distilled water and weighed portions of the respective ^{10}Be solution were then added to the samples. The total volume of each sample was about 16 mL. Four samples were prepared with the radioactive solution and two samples without active solution in order to measure the background counting rate (about 1 s^{-1}) which was then subtracted. The net counting rates of the radioactive samples were between 174 s^{-1} and 253 s^{-1}. As a quenching agent, nitromethane (CH_3NO_2) was used. All samples were shaken and centrifuged and then measured in a TriCarb 2800 TR and a Wallac 1414 Guardian^{TM}. Both counters consist of two-photomultiplier tubes with a coincidence circuit, and the quenching indicators *SQP*(*E*) and *tSIE* are automatically measured by means of the external sources of ^{152}Eu and ^{133}Ba, respectively [27].

The calibration curve, i.e. the counting efficiency of ^{3}H as a function of the quenching indicator, was measured with the aid of a PTB standard solution of ^{3}H, standardized by internal gas counting [28].

2.5.1 Efficiency calculations and determination of the activity concentration

The counting efficiencies were computed according to the CIEMAT/NIST method (see [27,29,30]), by means of a PTB code that comprises components of other programmes (see [31]). For a β emitter, the counting efficiency in a liquid scintillation counter with two photomultiplier tubes working in coincidence is given by

$$\varepsilon = \int_{0}^{E_{max}} S(E)(1-e^{-\frac{E\cdot Q(E)}{2\cdot M}})^{2} d \quad , \tag{1}$$

where *S*(*E*) is the normalized electron spectrum from the β decay, *Q*(*E*) is the ionization quenching function and *M* is a free parameter. The free parameter is determined by means of measurements of a ^{3}H solution with well-known activity concentration.

The spectrum *S*(*E*) is calculated according to the Fermi theory of the β decay, taking into account shape-factor functions. The β^- transition of ^{10}Be is of a unique 2nd forbidden nature, and the end-point energy is 555.8(6) keV [32]. The shape-factor function of ^{10}Be was recently confirmed by [33], and it induces a shift to the high-energy part of the spectrum yielding a high counting efficiency.

The ionization quenching function *Q*(*E*) was calculated by means of the procedures described in a previous article [34], taking into account the atomic composition of the samples. An ionization quenching parameter *kB*=0.0110 cm/MeV was used.

The determined ^{10}Be counting efficiencies are about 0.995 with a relative standard uncertainty of $2.3\cdot10^{-5}$ and the results are rather robust, i.e. changes of the input parameters as the end-point energy or the ionization quenching parameter have a relatively low influence on the final result. The measured counting rates of the samples were stable during the whole two-week period of observation. The results were also in good agreement when the counting efficiency was varied by means of chemical quenching. A detailed uncertainty budget for the activity concentration of one solution is given in Table 6. The solution masses were measured at PTB, and the masses determined when filling the ampoules were confirmed. Thus, any loss of solution as well as an increase of the activity concentration due to losses of inactive material can be excluded. Finally, the empty ampoules were flushed three times with about 1 mL of distilled water which was then measured by means of liquid scintillation counting. The remaining activities were found to be in the order of 1 Bq, and thus problems due to adsorption are considered to be small. In preliminary studies, we observed large adsorption losses when using glassware which had not been pre-treated with an inactive carrier solution.

3. Results

3.1 ^{10}Be/^{9}Be of master solution

Several dilutions produced from the master solution were measured for their ^{10}Be/^{9}Be ratio via the method described above. The dilution factors of these solutions relative to dil1 are presented in Table 8. A total of 50 ratio measurements were performed in two different sessions in March 2007 and December 2007 respectively (Table 7 and Fig. 4). These measurements cover a wide range of solute concentrations, resulting beam intensities, and collector set-ups (Tables 2, 3, 7, 8). The average ^{10}Be/^{9}Be is 1.736 ± 0.013 (Table 7). Employing the correction factor for mass bias (section 2.4.2), the original ^{10}Be/^{9}Be ratio of the master solution is 1.464 ± 0.014.

3.2 ^{10}Be concentration

^{10}Be concentrations in the solution measured for activity have been calculated using the following isotope dilution equation:

$$^{10}\mathrm{Be} = \frac{^{9}\mathrm{Be}_{S}}{\left(R_{mix} - R_{master}\right) \times F}$$

where R_{mix} is the measured ^{9}Be/^{10}Be isotope ratio, R_{master} is the measured ^{9}Be/^{10}Be ratio of the dilutions of the master solution before the addition of ^{9}Be (measured previously), F is the mass discrimination factor, and $^{9}\mathrm{Be}_{S}$ is the amount of ^{9}Be added to the respective solution from the ^{9}Be spike. The three different sets of isotope dilution series (dil2 to dil4) were each spiked with four (dil2) and two (dil3 and dil4) additions of ^{9}Be (Table 8). Figure 5 shows the variation of ^{10}Be/^{9}Be measured as a function of the ^{9}Be added. The excellent linear alignment of the data and the intercept that agrees with the measured ^{10}Be/^{9}Be of the master solution shows that ratio measurements were accurate and not affected by non-linear counting efficiencies. After application of the different dilution factors, the ^{10}Be concentration of solution used for the activity measurement (dil1) is $(1.0538 \pm 0.0080) \cdot 10^{17}$ atoms·g^{-1}. Note that the uncertainty of the concentrations calculated in Table 8 do not contain the error of the fractionation factor F. This factor has been propagated on the final calculation of the ^{10}Be half-life, however.

3.3 Activity determination

The activity concentration on 1st January 2008 for the two solutions, dil1 and dil2, were found to be (1662 ± 3) Bq/g and (347.6 ± 0.47) Bq/g, respectively (Table 8). The activity of dil1 has also been calculated using the results for dil2 and applying the dilution factor of that solution from dil1. As can be seen in Table 8, the results are in good agreement. The deviation of less than 1% might be due to the dilution process. Thus, the average of both values and a conservative uncertainty, (1670 ± 8) Bq/g is used as the final value of the activity concentration of dil1, which is then used for the calculation of the half-life.

4. ^{10}Be half-life and conclusions

To calculate the half-life we used the measured ^{10}Be concentrations of solutions dil1 and dil2 and the activity measurements of these solutions. The overall uncertainty comprises the uncertainty of the dilution factor determined by weighing, the statistical uncertainty of MC-ICP-MS measurements, the systematic uncertainty assigned to the determination of the mass discrimination factor and the uncertainty of the activity determination. These calculations result in a half-life of ^{10}Be of 1.386 My with a standard uncertainty of 0.016 My.

This new half-life has a lower uncertainty than previous estimates even using conservative uncertainties in part of the calculation (mass discrimation factor), but it is in agreement with the values of (1.36 ± 0.07) My [10] and (1.43 ± 0.10) My [11] and with the value recommended by the NIST (SRM-4325) standard [8].

Furthermore we have measured an absolute and accurate ^{10}Be/^{9}Be ratio of 1.464 with a standard uncertainty of 0.014, including the uncertainty component assigned to the mass discrimination correction factor, for the master solution.

In a parallel study using a fully independent set of experiments [35] have also determined the ^{10}Be half life. The isotope ratio measurements made in that study are based an Elastic Recoil Detection (ERD). The ^{10}Be/^{9}Be ratio obtained is 1.4791 ± 0.0068, which is in agreement with the ratio obtained in our study by ICP-MS. This solution can now serve as the starting material for new absolute AMS ratio standards.

Korschinek et al. [35] have furthermore performed an independent measurement of the master solutions activity. The half life resulting from the Munich study is (1.388± 0.018) My. Both these estimates are in excellent agreement. A weighted mean of the estimates of both new studies results in a half life of (1.387 ± 0.012 My). We recommend the use of this ^{10}Be half-life in future studies.

The method used here could potentially be used for other radioactive isotopes as well. Finally, unlike previous determinations, our half-life experiment provides a full internally self-consistent set of experiments, and does not rely on previous counting experiments involving potential dilution errors. We strongly recommend the use of this ^{10}Be half-life for the studies to come in the future.

Acknowledgments

We are grateful to Gunther Korschinek for providing the ^{10}Be/^{9}Be master solution. Prof. Michel at ZSR is thanked for radiochemical advice, Karin Hotz and Thomas Walczyk at ETH Zürich for allowing the use of their MC-ICP-MS, Frederic Malacrida and Jost Eikenberg at PSI, Villigen, for their help in sample shipment. We want to acknowledge T. Dunai for his efforts to conduct CRONUS-EU. This work is a contribution of EU Marie Curie Network CRONUS-EU.

REFERENCES

[1] D.J. Hughes, C. Eggler, and C.M. Huddleston, The Half-Life of Be-10, Phys. Rev. 71 (1947) 269-269.

[2] E.M. McMillan, Energy and Half-Life of the Be-10 Radioactivity. Phys. Rev. 72 (1947) 591-593.

[3] J.F. Emery, E.I. Wyatt, G.I. Gleason, and S.A. Reynolds, Half-lives of Radionuclides .4, Nucl. Sc. Engin. 48 (1972) 319-&.

[4] E.M. McMillan, Correction. Phys. Rev. C, 6 (1972) 2296-2296.

[5] F. Yiou and G.M. Raisbeck, Half-Life of Be-10, Phys. Rev. Let. 29 (1972) 372-375.

[6] T. Makino, R. Gensho and M. Honda, Preparation of ^{10}Be and the Measurement of Isotopic Ratio of Beryllium, Massspectroscopy (JMSSJ) 23 (1975) 33-39.

[7] H.J. Hofmann, J. Beer, G. Bonani, H.R. Von Gunten, S. Raman, M. Suter, R.L. Walker, W. Wölfli, and D. Zimmermann, Be-10: Half-life and AMS-Standards, Nucl. Instr. Meth. B 29 (1987) 32-36.

[8] K.G.W. Inn, S. Raman, B.M. Coursey, J.D. Fassett and R.L. Walker, Development of the NBS Be-10/Be-9 Isotopic Standard Reference Material, Nucl. Instr. Meth. B 29 (1987) 27-31.

[9] R. Middleton, L. Brown, B. Dezfoulyarjomandy and J. Klein, On ^{10}Be Standards and the Half-life of ^{10}Be, Nucl. Instr. Meth. B 82 (1993) 399-403.

[10] K. Nishiizumi, M. Imamura, M.W. Caffee, J.R. Southon, R.C. Finkel, J. McAninch, Absolute calibration of Be-10 AMS standards, Nucl. Instr. Meth. B 25 (2007) 403-413.

[11] D. Fink, and A. Smith, An inter-comparison of Be-10 and Al-26 AMS reference standards and the Be-10 half-life, Nucl. Instr. Meth. B 259 (2007) 600-609.

[12] D.E. Granger, A review of burial dating methods using ^{26}Al and ^{10}Be. In: L.L. Siame, D.L. Bourles and E.T. Brown (Editors), In situ-produced cosmogenic nuclides and quantification of geological processes. Geological Society of America (2006) 1-16.

[13] N.S. Belshaw, R.K. O'Nions, F. von Blanckenburg, A SIMS method for ^{10}Be/^{9}Be ratio measurement in environmental materials, Int. J. Mass Spect. Ion Proc 142 (1995) 55-67.

[14] F. von Blanckenburg, N.S. Belshaw, and R.K. O'Nions, Separation of ^{9}Be and cosmogenic ^{10}Be from environmental materials and SIMS isotope dilution analysis, Chem. Geol. 129 (1996) 93-99.

[15] F. von Blanckenburg, T. Hewawasam and P.W. Kubik, Cosmogenic nuclide evidence for low weathering and denudation in the wet, tropical highlands of Sri Lanka, J. Geophys. Res.-Earth Surf. 109 (2004) F03008.

[16] Y.I. Taylor, and H.C. Urey, Fractionation of the Li and K isotopes by chemical exchange with zeolites. J. Chem. Phys. 6 (1938) 429-438.

[17] A.D. Anbar, J.E. Roe, J. Barling, K.H. Nealson, Nonbiological fractionation of iron isotopes, Science 288 (2000) 126-128.

[18] T. Moriguti, E. Nakamura, High-yield lithium separation and the precise isotopic analysis for natural rock and aqueous samples, Chem. Geol. 145 (1998) 91-104.

[19] S. Weyer, and J. Schwieters, High precision Fe isotope measurements with high mass resolution MC-ICP-MS, Int. J. Mass Spect. 226 (2003) 355-368.

[20] G.R. Gillson, D.J. Douglas, J.E. Fulford, K.W. Halligan and S.D. Tanner, Non spectroscopic Interelement Interferences in Inductively Coupled Plasma Mass-Spectrometry. Anal. Chem.60 (1988) 1472-1474.

[21] S.D. Tanner, Space-Charge in ICP-MS - Calculation and Implications, Spectrochim. Acta Part B Atom. Spectr. 47 (1992) 809-823.

[22] J. Woodhead, A simple method for obtaining highly accurate Pb isotope data by MC-ICP-MS, J. Anal. Atom. Spect. 17 (2002) 1381-1385.

[23] F. Albarède, P. Telouk, J. Blichert-Toft, M. Boyet, A. Agranier and B. Nelson, Precise and accurate isotopic measurements using multiple-collector ICP-MS, Geochim. Cosmochim. Acta 68 (2004) 2725-2744.

[24] R. Schoenberg and F. von Blanckenburg, An assessment of the accuracy of stable Fe isotope ratio measurements on samples with organic and inorganic matrices by high-resolution multicollector ICP-MS, Int. Journ. Mass Spect. 242 (2005) 257-272.

[25] C.N. Marechal, P. Telouk and F. Albarède, Precise analysis of copper and zinc isotopic compositions by plasma-source mass spectrometry, Chem. Geol. 156 (1999) 251-273.

[26] I.V. Chernyshev, A.V. Chugaev, K.N. Shatagin, High precision Pb isotope analysis by multicollector-ICP-mass spectrometry using ^{205}Tl/^{203}Tl normalization: Optimization and calibration of the method for the studies of Pb isotope variations, Chem. Int. 45 (2007) 1065-1076.

[27] R. Broda, P. Cassette, K. Kossert, Radionuclide Metrology using Liquid Scintillation Counting. Metrologia 44 (2007) S36-S52

[28] E.W. Günther, Das Gasfüllzählrohr der PTB – eine Apparatur zur Bestimmung der Aktivität radioaktiver Gase. PTB-Report PTB-Ra-32 (1993) ISBN 3-89429-415-9.

[29] B.M. Coursey, W.B. Mann, A. Grau Malonda, E. Garcia-Toraño, J.M. Los Arcos, J.A.B. Gibson, D. Reher, Standardization of carbon-14 by 4πβ liquid scintillation efficiency tracing with hydrogen-3, Int. J. Appl. Radiat. Isot. 37 (1986) 403-408.

[30] A. Grau Malonda, Free parameter models in liquid scintillation counting. Colección Documentos Ciemat (Madrid) (1999) 1-416.

[31] K. Kossert and H. Schrader, Activity standardization by liquid scintillation counting and half-life measurement of ^{90}Y, Appl. Radiat. Isot. 60 (2004) 741-749.

[32] G. Audi, A.H. Wapstra, The 1995 update to the atomic mass evaluation, Nucl. Phys A 59 (1995) 409-480.

[33] A. Grau Carles, K. Kossert, Measurement of the shape-factor functions of the long-lived radionuclides ^{87}Rb, ^{40}K and ^{10}Be, Nucl. Instr. Meth. A 572 (2007) 760-767.

[34] K. Kossert and A. Grau Carles, Study of a Monte-Carlo rearrangement model for the activity determination of electron-capture nuclides by means of liquid scintillation counting, Appl. Radiat. Isot. 66 (2008) 998-1005.

[35] G. Korschinek, A. Bergmaierb, T. Faestermanna, U.C. Gerstmannc, K. Kniea, G. Rugela, A. Wallnerd, I. Dillmanna, G. Dollingerb, Ch. Lierse von Gostomskie, K. Kossertf, M. Maitia, M. Poutivtseva and A. Remmer, A new value for the half-life of 10Be by heavy ion elastic recoil detection and liquid scintillation counting , Nucl. Instr. Meth Res. B (2009) doi: 10.1016/j.nimb.2009.09.020

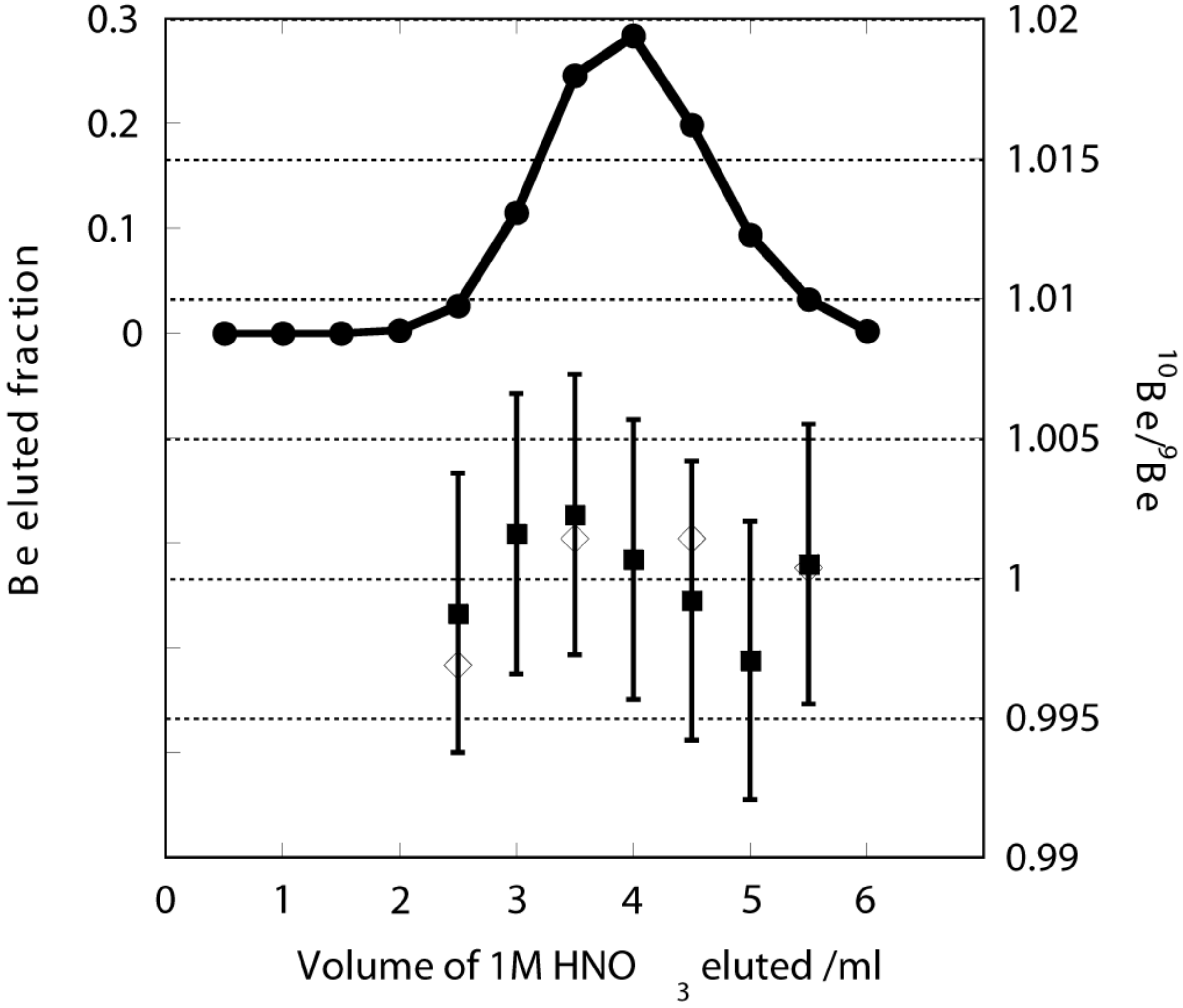


Figure 1: Fraction of Be eluted from a 1mL cation exchange column (resin Biorad AG50-X8, 1M HNO_3) used to purify the master solution from its boron. Black circles show the eluted fraction (left axis). All ^{10}Be/^{9}Be ratios are normalised to unity. Black squares show the ^{10}Be/^{9}Be ratio of the fraction eluted via MC-ICP-MS; the bars indicate standard uncertainties. Open diamonds represent the ^{10}Be/^{9}Be measurements of a diluted aliquot of the master solution used as a standard for comparison (uncertainties not shown but same order as fraction measurements).

Figure 2:

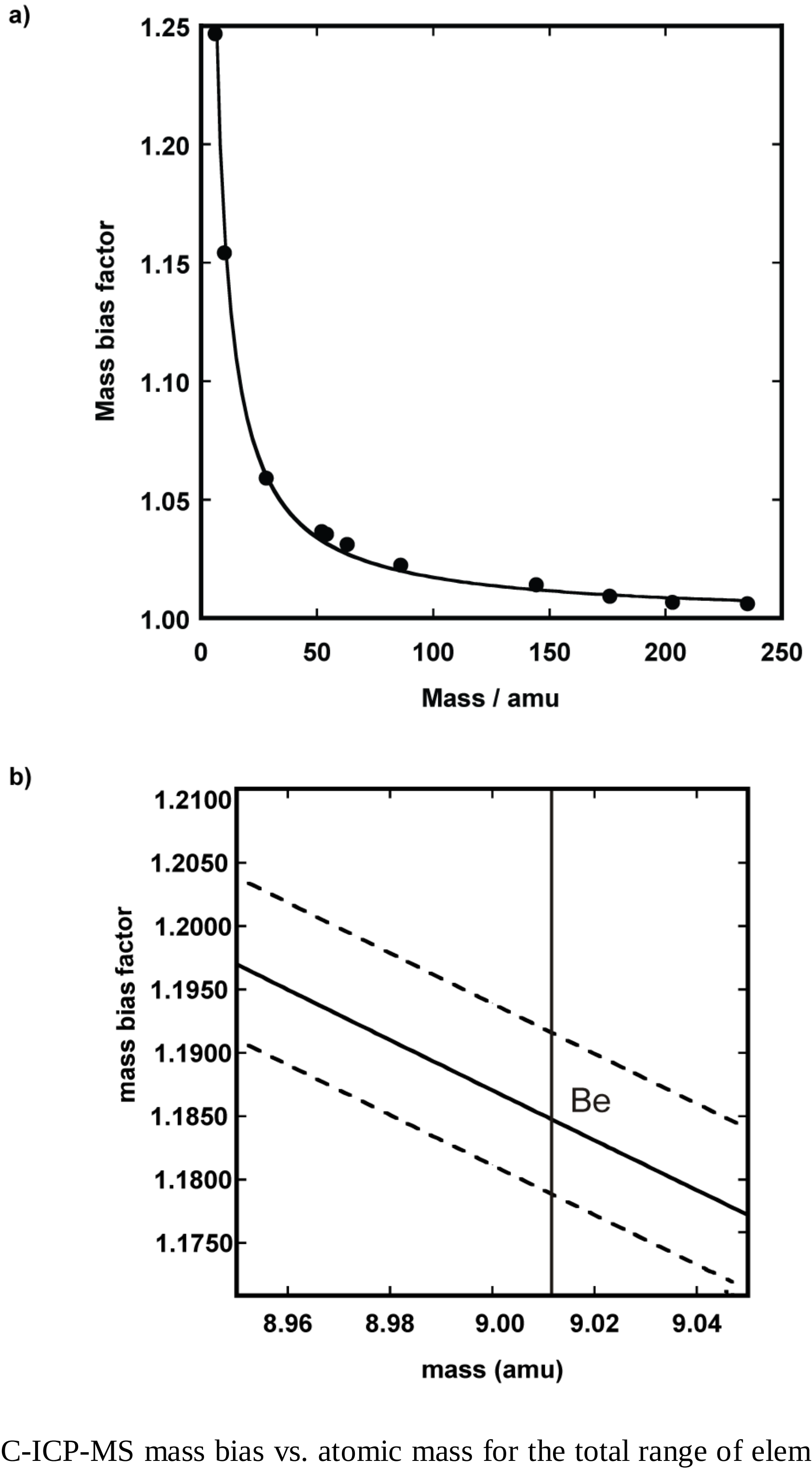
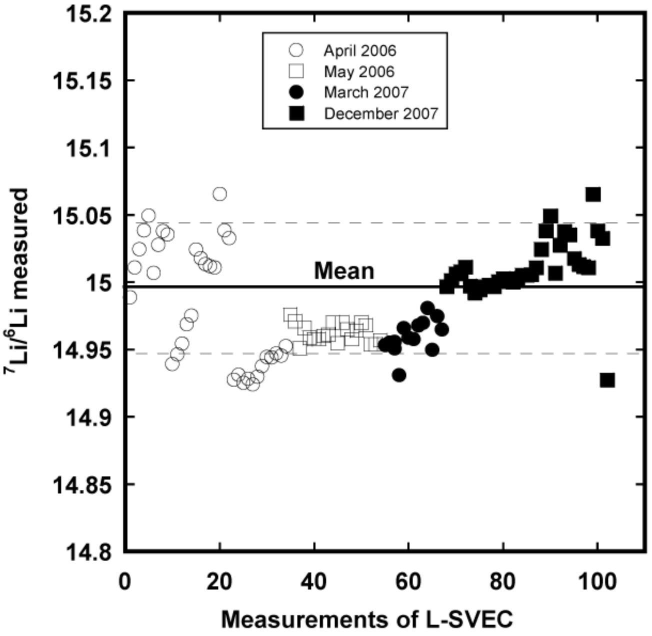


Figure 2: a) MC-ICP-MS mass bias vs. atomic mass for the total range of elements typically measured on a Neptune MC-ICP-MS (uncertainties are reflected by the size of the points);

b) shows a close-up of the Be mass range. The circles represent the range of mass bias typically encountered in the same mass spectrometric set-up as that used here. A power law permits the calculation of a mass bias for this specific machine. The solid curve is the best fit for this power law whereas the dashed lines show the lowest and highest possible range of variation determined by means of Monte Carlo simulation.

Figure 3:

a)



b)

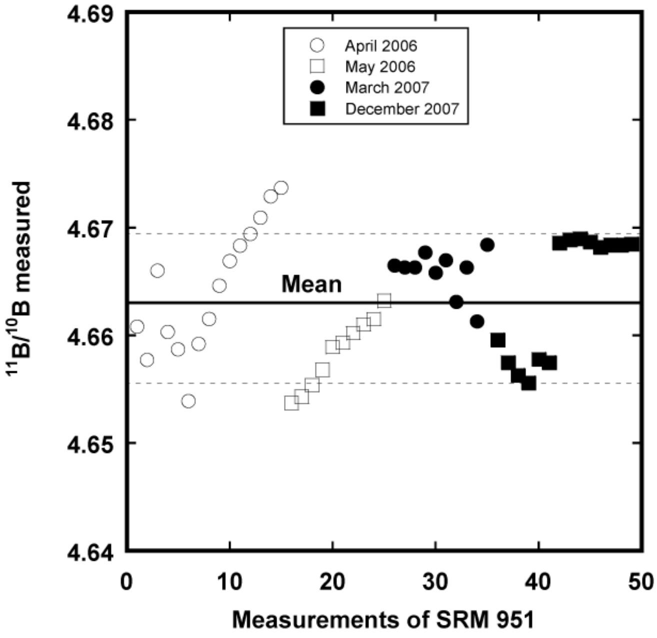


Figure 3: a) ^{7}Li/^{6}Li vs. number of measurement of L-SVEC standard (IAEA); b) ^{11}B/^{10}B vs. number of measurement of SRM951 (NIST) standard. Both plots show the variations on isotope ratios measured under different conditions, leading to the variation on mass bias for these elements.

Figure 4:

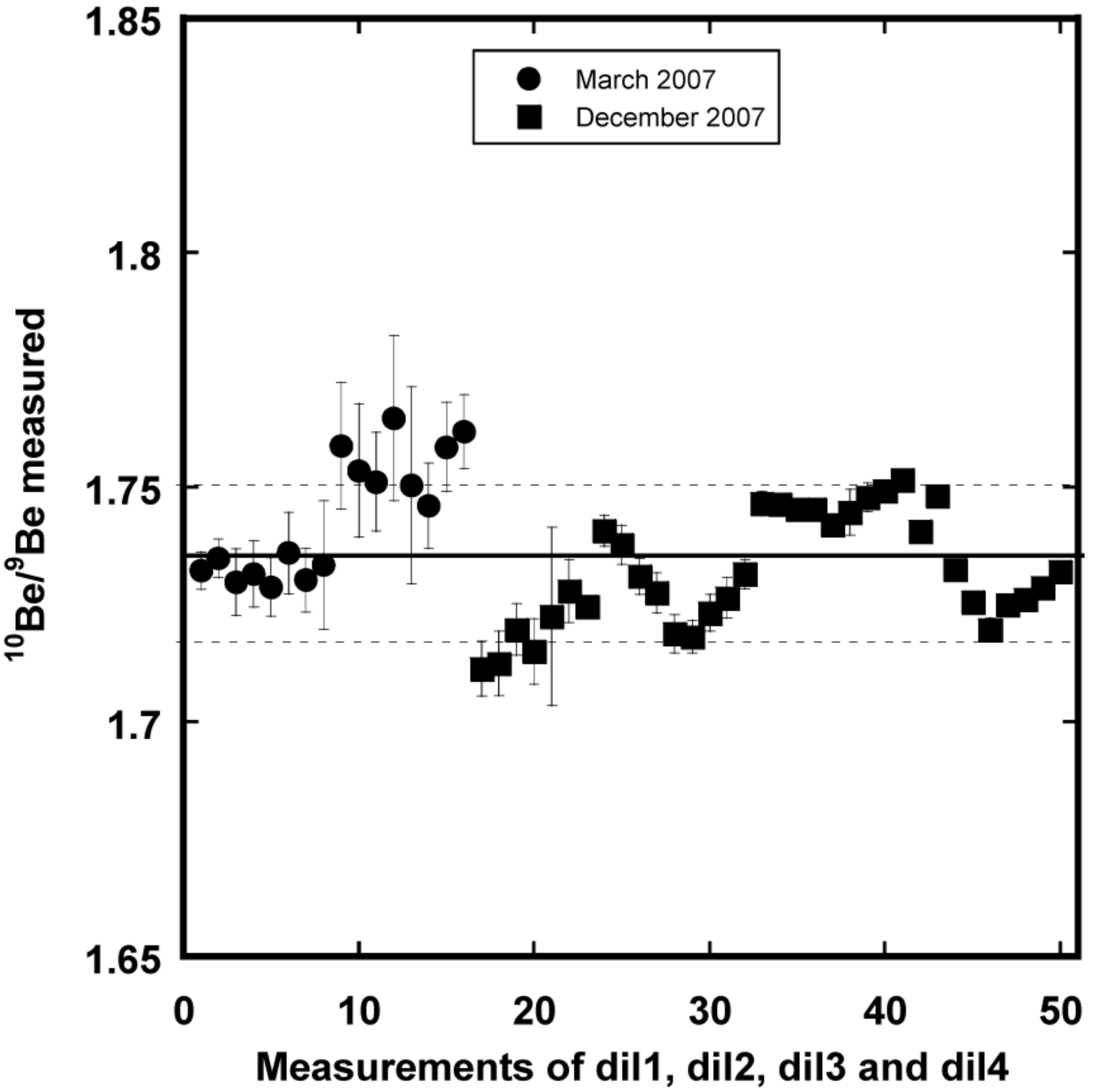


Figure 4: All measurements of ^{10}Be/^{9}Be ratios in the unspiked dilutions (dil1, dil2, dil3, dil4) within two sessions (black circles for March 2007 and black squares for December 2007). The bars correspond to the standard deviation (20 cycles). The dashed lines indicate the standard deviation of the mean, which is 0.013.

Figure 5:

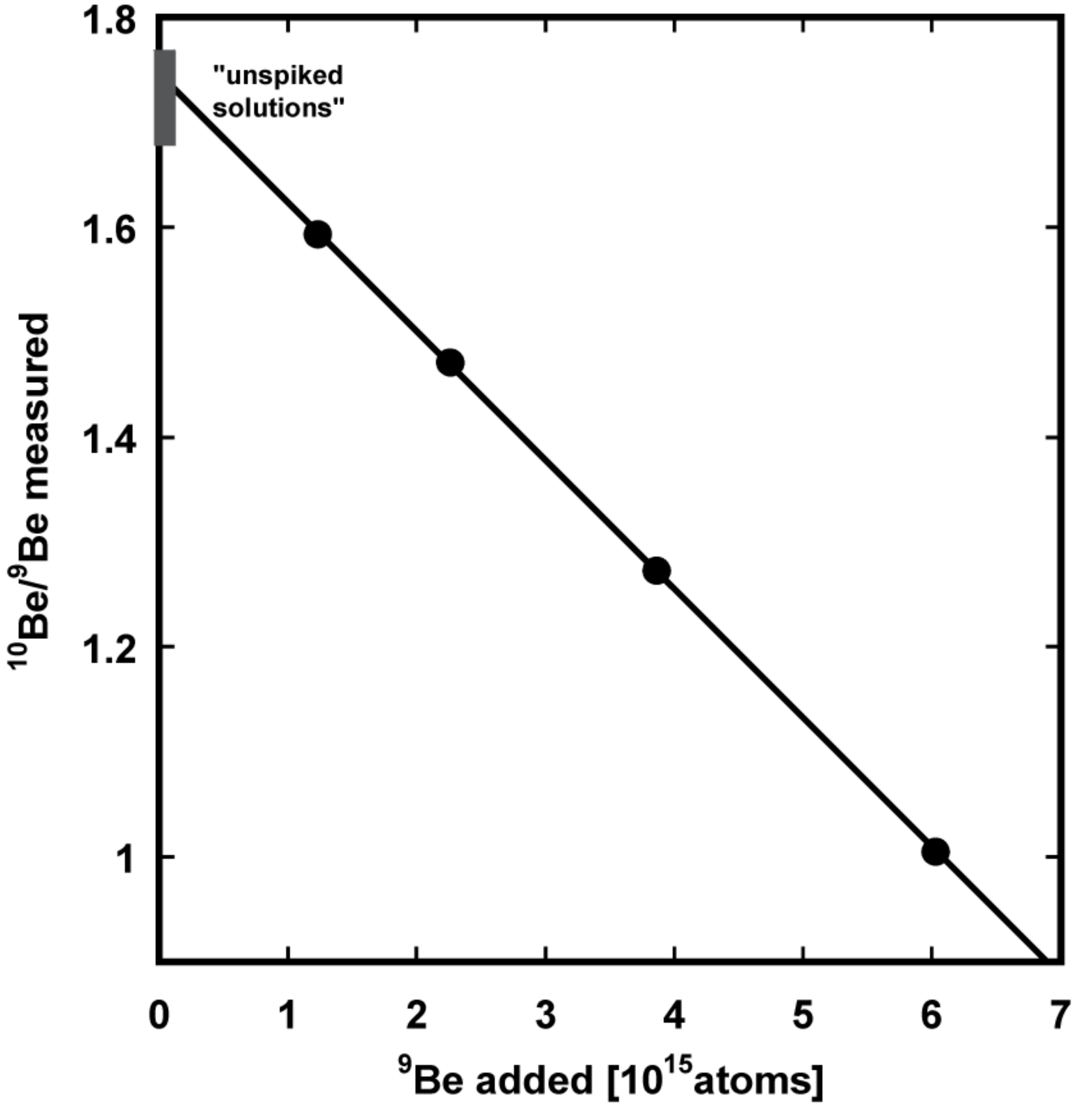


Figure 5: ^{10}Be/^{9}Be measured vs. ^{9}Be atoms added (isotope dilution) dil2 (see Table 8 for values). Uncertainties are reflected by the size of the points. The bar shows the range of ^{10}Be/^{9}Be measurements of the unspiked solutions (Fig 4 and Table 7)

Table 1: ^{10}Be half-life determinations.

Half-life of ^{10}Be in 10^6 years	Standard uncertainty in 10^6 years	Reference
2.9	-	[1]
2.5	0.5	[2]
1.6	0.2	[3]
1.3	-	[3]
1.9	-	[3]
1.7	0.4	[4]
1.5	0.3	[5]
1.48	0.15	[6] in [7]
1.34	0.07	[8]
1.51	0.06	[7]
1.53	0.07	[9]
1.36	0.07	[10]
1.43	0.1	[11]
1.388	0.018	Korschinek et al. (in prep)
1.386	**0.016**	**This work**

Table 2: ICP collector set-up

	cycle	**L2**	**Center Position**		**H2**	**collection time**
			C	**SEM**		
Faraday (F)	1		^{9}Be			2s
	2	^{10}Be+^{10}B			^{11}B	2s
	3		^{10}Be+^{10}B			2s
SEM+Faraday (SF)	1		^{9}Be			2s
	2	^{10}Be+^{10}B			^{11}B	2s
	3			^{9}Be		4s
	4			^{10}Be+^{10}B		4s
	5			^{11}B		4s
SEM (S)	1			^{9}Be		4s
	2			^{10}Be+^{10}B		4s
	3			^{11}B		4s

Table 3: Typical ion beam intensities for different collector set-ups in counts per second (cps).

	^{9}Be		^{10}Be+^{10}B		^{11}B
	min	max	min	max	
Wash solution (S) cps	1.3x10^{3}		4.2x10^{4}		2x10^{5}
Procedure blank (S) cps	1.5x10^{3}		5x10^{4}		2.4x10^{5}
Samples range(S) cps	5x10^{5}	7x10^{5}	5x10^{5}		2x10^{5}
Samples range (F) cps	5x10^{5}	2.7x10^{7}	5.2x10^{5}	5x10^{7}	2x10^{5}

Table 4: Instrumental operating conditions for the Neptune MC-ICP-MS

Extraction[V]:	-2000
Focus[V]:	-600
Cool Gas[l/min]:	14.6
Aux Gas[l/min]:	0.7
Sample Gas[l/min]:	0.7
RF Operating Power[W]:	1300
Cones	Nickel
Mass resolution	1100
Nebullizer type	Microflow (PFA)
Aspiration rate [µl.min^{-1}]	60
Spray Chamber	PEEK
Torch	Sapphire

Table 5: Mass discrimination for different elements measured on a Neptune MC-ICP-MS with wet nebulization.

	Standard used	atomic number	mass	isotope ratio studied	R certified	R measured	1σ %	$(R_{measured}/R_{certified})$ per amu	1σ
Li	L-SVEC	3	6.02	$^{7}Li/^{6}Li$	12.019	14.959	0.304	1.247	0.0031
B	SRM 951	5	10.01	$^{11}B/^{10}B$	4.044	4.663	0.115	1.153	0.0013
Si	IRMM-018	14	27.98	$^{29}Si/^{28}Si$	0.05077	0.05376	0.125	1.059	0.0030
Cr	SRM 3112a	24	51.94	$^{53}Cr/^{52}Cr$	0.1135	0.1176	0.219	1.038	0.0023
Fe	IRMM-014	26	53.94	$^{56}Fe/^{54}Fe$	15.699	16.835	0.131	1.036	0.0033
Cu	Merck	29	62.93	$^{65}Cu/^{63}Cu$	0.04451	0.04729	0.133	1.031	0.0022
Sr	SRM-987	38	85.91	$^{87}Sr/^{86}Sr$	0.713	0.73	0.098	1.023	0.0010
Nd	Neptune test sol.	60	144.25	$^{146}Nd/^{144}Nd$	0.7219	0.7427	0.123	1.014	0.0013
Hf	AMES	72	175.94	$^{177}Hf/^{176}Hf$	0.28	0.275	0.049	1.009	0.0005
Tl	SRM-997	81	202.97	$^{205}Tl/^{203}Tl$	2.389	2.422	0.212	1.007	0.0019
U	U950a	92	235.04	$^{238}U/^{235}U$	137.88	140.48	0.243	1.006	0.0008

Data for Tl from [26]; all other data have been measured in-house.

Table 6: Standard uncertainty components of the activity concentration *a* of a ^{10}Be solution measured by means of LSC

Component	$u(a)/a$ in %
Counting statistics	0.06
Weighing	0.03
Counting time (life time)	0.1
Background	0.05
Quenching	0.01
Impurities (no impurity detected)	< 0.05
Decay data and model	0.03
Tracer (^{3}H)	< 0.01
Square root of the sum of quadratic components (correlation coefficients are taken into account in the summation)	0.15

(components with $u(a)/a$ < 0.001 % are not listed).

Table 7: $^{10}Be/^{9}Be$ measurements of unspiked dilutions of the master solution.

solution	dil1			dil2						dil3						dil4		
date	December 2007			March 2007			December 2007			March 2007			December 2007			December 2007		
	$^{10}Be/^{9}Be$	SD %	coll.	$^{10}Be/^{9}Be$	SD %	coll.	$^{10}Be/^{9}Be$	SD %	coll.	$^{10}Be/^{9}Be$	SD %	coll.	$^{10}Be/^{9}Be$	SD %	coll.	$^{10}Be/^{9}Be$	SD %	coll.
	1.729	0.08	(F)	1.759	0.77	(F)	1.719	0.24	(F)	1.732	0.23	(F)	1.711	0.34	(F)	1.748	0.09	(S)
	1.732	0.07	(F)	1.753	0.81	(F)	1.718	0.20	(F)	1.735	0.24	(F)	1.712	0.40	(F)	1.732	0.11	(S)
				1.751	0.60	(F)	1.723	0.23	(F)	1.730	0.41	(F)	1.720	0.32	(F)	1.726	0.12	(S)
				1.765	1.00	(F)	1.726	0.25	(F)	1.731	0.41	(F)	1.715	0.41	(F)	1.720	0.14	(S)
				1.750	1.20	(F)	1.731	0.18	(F)	1.729	0.36	(F)	1.722	1.10	(F)			
				1.746	0.52	(F)	1.746	0.15	(F)	1.736	0.50	(F)	1.728	0.39	(F)			
				1.759	0.54	(F)	1.746	0.11	(F)	1.730	0.39	(F)	1.725	0.12	(F)			
				1.762	0.45	(F)	1.745	0.09	(F)	1.733	0.79	(F)	1.741	0.19	(F)			
							1.745	0.09	(F)				1.738	0.24	(S)			
							1.742	0.10	(F)				1.725	0.09	(S)			
							1.745	0.28	(F)				1.726	0.12	(S+F)			
							1.748	0.17	(F)									
							1.749	0.11	(F)									
							1.752	0.07	(F)									
							1.741	0.08	(F)									
Average±σ	1.730	*0.002*		1.756	*0.006*		1.738	*0.011*		1.732	*0.002*		1.724	*0.009*		1.731	*0.011*	
							1.744 ±	*0.013*					1.727 ±	*0.008*				
										1.736 ±	***0.013***							

Table 8: ^{10}Be concentrations, ^{10}Be/^{9}Be ratio, calculated ^{10}Be concentration and activity concentration, a.

	dilution factor from dil1	^{9}Be added in atoms x 10^{15}	total weighing error 1σ %	^{10}Be/^{9}Be measured	1σ	n	Collector setup	10Be concentration in dil1 in atoms x 10^{17}/g	1σ (10^{14})	specific activity in kBq/g
dil2	0.2071									0.34756±0.00047
dil2_9Be1	0.1884	1.230	0.19	1.59	0.002	4	(F)	1.068	7.76	
dil2_9Be2	0.1727	2.259	0.12	1.47	0.004	5	(F)	1.064	7.58	
dil2_9Be3	0.1483	3.861	0.15	1.27	0.005	5	(F)	1.047	7.51	
dil2_9Be4	0.1153	6.026	0.13	1.01	0.003	5	(F)	1.052	7.51	
dil3	0.2005									
dil3_9Be1	0.0208	6.776	0.09	0.31	0.001	5	F	1.051	7.44	
dil3_9Be2	0.0139	9.055	0.13	0.17	0.001	5	F	1.053	7.52	
dil4	0.0208									
dil4_9Be1	0.0042	2.609	0.23	0.93	0.003	5	3(F)+ 2(SF)	1.042	7.70	
dil4_9Be2	0.0042	4.855	0.22	0.66	0.002	7	4(F)+3(SF)	1.051	7.73	
dil1								*1.054*	*7.97*	1.662±0.003
dil1 from dil2										1.678±0.004
average dil1										1.670±0.008

The uncertainty of the 10Be concentrations are calculated without the systematic uncertainty assigned to the mass discrimination factor (see text).