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Measurement of carrier-free ^{10}Be samples with AMS: the method and its potential

C. Maden [a,*], M. Döbeli [b], P.W. Kubik [b], M. Frank [c], M. Suter [a]

[a] *Institute of Particle Physics, ETH Hönggerberg, CH-8093 Zürich, Switzerland*
[b] *Paul Scherrer Institut, c/o ETH Hönggerberg, CH-8093 Zürich, Switzerland*
[c] *Institute of Isotope Geology and Mineral Resources, ETH-Zentrum, CH-8092 Zürich, Switzerland*

Abstract

A method for direct measurement of the natural ^{10}Be/^{9}Be ratio in a sample by AMS is presented. Samples of 100 ng of Be with ^{10}Be concentrations orders of magnitude higher than in conventional ^{10}Be AMS samples were produced without the addition of ^{9}Be carrier and analysed using the accelerator secondary ion mass spectrometry (Accelerator SIMS) source of the PSI/ETH AMS facility. Special mounting techniques and the analysis procedure using a focussed Cs^+ beam of up to 600 nA and beam spot diameter of 100 μm are described.

The results of measurements on two test samples from Pacific ferromanganese crust D11–1 are presented and compared with similar measurements by conventional secondary ion mass spectrometry (SIMS). Background measurements at a level of $\sim 5\times10^{-11}$ indicate that ratios of a few times 10^{-10} could be measured to a precision of ~10%.

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1. Introduction

The cosmogenic nuclide ^{10}Be has found many applications as a tracer in environmental science over the last two decades and is one of the radionuclides most frequently measured with AMS. Although it is mostly the ^{10}Be concentration in the original sample that is of interest, there are applications in which the abundance of cosmogenic ^{10}Be relative to terrestrial ^{9}Be provides important information [1,2]. One such application that will be addressed in the following is the measurement of the ^{10}Be/^{9}Be ratio as a function of depth in ferromanganese crusts. With this information growth rates of crusts are determined and past oceanographic events reflected by changes in the radiogenic isotope composition in the crusts are dated [3,4].

Because of the relatively low concentration of ^{9}Be in ferromanganese crusts (1–10 ppm), sample sizes are too small (~100 ng of ^{9}Be) to be analysed

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[*] Corresponding author. Present address: Scottish Universities Environmental Research Centre, Scottish Enterprise Technology Park, East Kilbride G75 0QF, UK. Tel.: +44-1355-270-179; fax: +44-1355-229-898.
E-mail address: c.maden@suerc.gla.ac.uk (C. Maden).

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with methods presently used in conventional AMS. But due to the high sensitivity of AMS several hundred micrograms of ^{9}Be carrier can be added to the sample during chemical pre-concentration bringing the sample size into the range measurable with AMS. However, this way information on the natural ^{10}Be/^{9}Be ratio is lost and can only be obtained by performing an additional measurement of the ^{9}Be concentration in the sample, for example with inductively coupled plasma mass spectrometry (ICP-MS), which introduces additional uncertainty in determination of the ^{10}Be/^{9}Be ratio. To avoid this, the direct measurement of the natural ^{10}Be/^{9}Be ratio has been explored using the Accelerator SIMS source at the PSI/ETH AMS facility.

2. Sample preparation and loading

For each sample 30–100 mg of material was taken from the ferromanganese crust. Chemical purification and pre-concentration of the Be followed a previously published method [5] with some modifications, mainly a miniaturisation and a reduction to the first two column separation steps. Additional information on the chemical method can be obtained from the authors and will also be described in more detail in a subsequent publication. It enables a high-purity separation of nanogram amounts of beryllium from the matrix of the ferromangenese crust. At the end of chemical pretreatment the samples are evaporated in 7 ml-Teflon vials.

Following dissolution in 1–3 μl of 65% HNO_3 the samples were pipetted onto stainless steel wafers held at a temperature of 65 °C. The dimensions of the wafer are $24\times24\times0.1$ mm and stainless steel was chosen because of its hydrophilic surface allowing the pipetted drops to disperse on the surface thereby distributing the beryllium evenly over the wafer after the solvent has evaporated. The resulting spots of beryllium are 2–3 mm in diameter. A second reason for the choice of stainless steel is its resistance to high temperatures and the solvent acid. The beryllium is deposited on the wafer as $BeNO_3$ and by baking it at 850 °C for 2 h the beryllium nitrate decomposes to beryllium oxide.

For sample sizes of ~100 ng the area over which the drop disperses has to be limited by creating a hydrophobic ring around a hydrophilic area of about 1 mm diameter. This is done by heating the wafer to 225 °C and then drawing a ring by hand on the surface of the wafer with the end of a plastic capillary tube usually used for pipetting μl-amounts of liquid. 225 °C is sufficient for the plastic to change the hydrophilic properties of the steel surface, but still low enough for the plastic not to melt completely. The plastic ring subsequently evaporates in the baking process.

Controlling the size of the area over which the sample is allowed to disperse is important because the beryllium has to be distributed evenly over the surface of the wafer, but at the same time a certain thickness of the beryllium layer is necessary. The analysis time available before the primary beam has sputtered through the beryllium layer and has to be moved to a fresh spot on the sample increases with the thickness of the layer. On the other hand, mounds or an uneven structure of beryllium on the plane surface of the stainless steel will cause different ion optical conditions for different positions of the primary beam on the sample. The mass fractionation that is caused by this can be as large as a few percent.

For this experiment only one unknown sample was pipetted onto a single stainless steel wafer. In addition, standards and blanks were pipetted onto the same wafer as the unknown sample. Due to the larger amounts of beryllium in standards and blanks the hydrophobic ring on the steel surface is not necessary. The standard used for the measurements presented here is the M3 fraction of the dilution series published by Hofmann et al. [6] with a nominal ^{10}Be/^{9}Be ratio of 3.64×10^{-8}. This standard is dissolved in 0.1 M HCl, an acid that readily corrodes stainless steel during the baking process. To reduce corrosion the standard, consisting of 1 μl of original M3 solution, was evaporated at 150 °C in a Teflon vial before being redissolved in 2 μl of 65% HNO_3 and transferred to the wafer. 1 μl of the blank solution (1000 ppm ^{9}Be carrier solution routinely used for ^{10}Be AMS) was pipetted directly onto the wafer. Because the beryllium is dissolved in 0.5 M HNO_3, no pretreatment of this solution was necessary.

Since the beam spot of the primary beam is a lot smaller than the size of the sample, the electrically insulating beryllium oxide has to be made conducting so that charging of the sample is not a problem during analysis. To achieve this the entire stainless steel wafer with the samples on it is covered with a 20 nm thick, electrically conducting layer by evaporating high purity gold onto it.

3. Instrumentation

The samples were measured with a focussed, mass filtered caesium beam from the Accelerator SIMS source that has been installed at the PSI/ETH AMS facility. It produces up to 600 nA of Cs^+ current focussed to a spot with a diameter of 100 μm. The resulting secondary ion currents are about three orders of magnitude smaller than those produced by high current sources used for conventional ^{10}Be AMS measurements meaning that three orders of magnitude smaller amounts of beryllium oxide can be analysed for long enough to measure the natural $^{10}Be/^{9}Be$ ratio to a precision of a few per cent. Details of the ion source used for the measurements presented in this work have been published elsewhere [7,8].

Fig. 1 shows a cross section through the sputter chamber of the Accelerator SIMS source. The focussed caesium gun sits on top of the chamber while the secondary ions are extracted at an angle of 60° relative to the caesium beam. The design and geometry of the sample stage require that samples are of a wafer-like shape with a plane surface of about 20×20 mm in size. The position of the Cs beam on the wafer is monitored using a video camera with a macro objective, making it possible to find the position of the samples even after they have been gold coated.

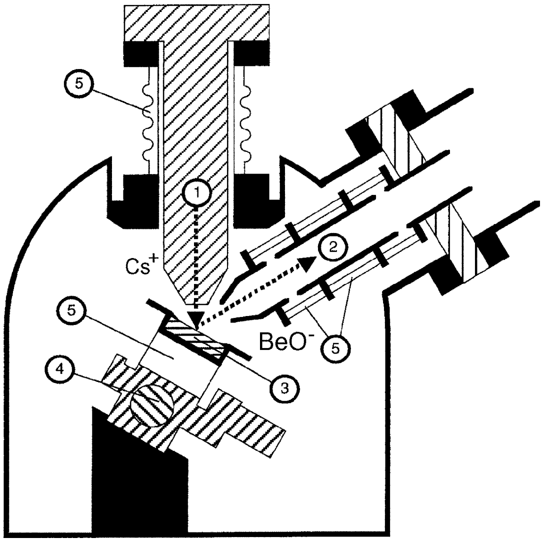

Fig. 1. Cross section through the sputter chamber of the Accelerator SIMS facility: (1) focussed Cs beam source, (2) secondary ion extraction, (3) sample holder, (4) x/y stepping motor stage, (5) insulators.

The only difference between the setup of a routine ^{10}Be AMS measurement performed at the PSI/ETH AMS facility and the measurement of carrier-free ^{10}Be samples is the use of a different ion source. BeO^- ions are extracted from the ion source and the switching system of the low energy magnet injects mass 25 and 26 amu sequentially into the tandem accelerator, which is run at 5.6 MV with a gas stripper. As in routine measurements, the current of $^{16}O^{5+}$ fragments from the break-up of the $^{9}Be^{16}O^-$ molecule is measured in a Faraday cup following the analysing magnet and used for normalisation. The $^{10}Be^{3+}$ beam passes through a second stripping foil and a second magnetic deflection to reduce the ^{10}B isobaric interference, taking advantage of the different charge state distribution at the higher energy. The remaining ^{10}B in the beam is stopped in a gas absorber just in front of the gas ionisation detector.

Fig. 2 shows the relevant parts of the low energy side of the PSI/ETH AMS facility. When setting up the AMS system for carrier free ^{10}Be analysis, the high current source, with its cathode potential set to match the sample potential of the Accelerator SIMS source, is used to tune the system. Once the facility is tuned, the high current source is turned off and the electrostatic deflector just after the source (ED 3) is retracted out of the beam line. The integrator used to measure the $^{16}O^{5+}$ current is changed to one suitable for the measurement of 100 pA-currents and the pulse of the beam bouncing system, during which $^{9}Be^{16}O^-$ is injected into the accelerator, is increased by a factor of 10. Except for minor retuning of the low energy magnet, none of the settings of the ion optical

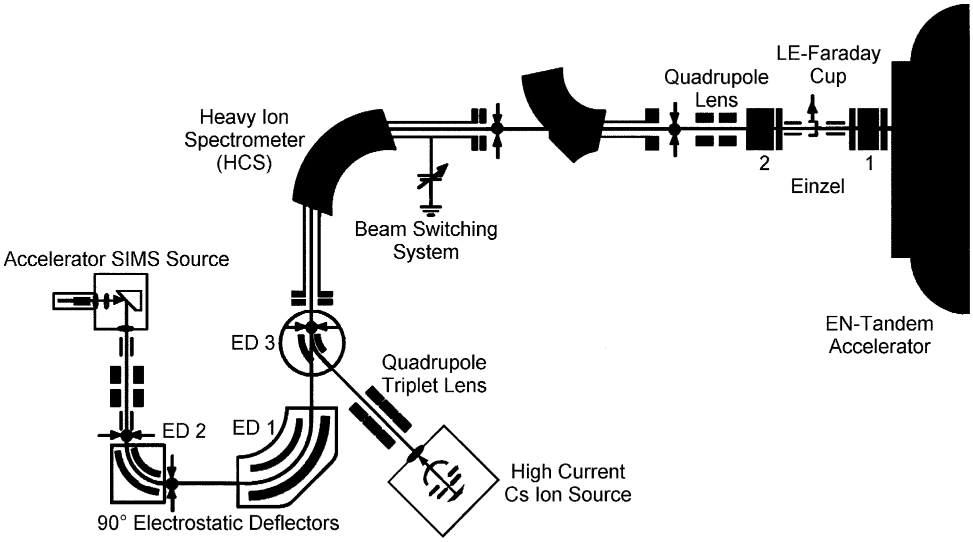

Fig. 2. Ion sources on the low energy side of the PSI/ETH AMS facility that are relevant for this work.

elements tuned with the high current source are changed during measurement.

With the facility tuned and ready for analysis the stainless steel wafers prepared as described in Section 2 are brought into the Accelerator SIMS source one by one. With the *x*/*y*-stage the sample to be measured is placed under the primary beam and extraction of the secondary ions is optimised by adjusting the steerers and lenses in the extraction of the source. Once this has been done the extraction unit is left unchanged until the next wafer is brought into the chamber thus assuring identical analytical conditions for all the samples on a given wafer and minimising mass fractionation between individual measurements.

The measurement procedure of a wafer is as follows. First a blank sample is measured to determine the background. Then alternately the sample and the standard are measured three times for approximately 10 min each. Fig. 3 illustrates a typical measurement of 10 min length by plotting the ^{10}Be counting rate and $^{16}O^{5+}$ current together with the resulting ^{10}Be/^{9}Be ratio as a function of time. For technical reasons this particular measurement was performed with a Cs^+ current of about 100 nA. The strong increase in current after about 450 s is caused by moving the sample under the caesium beam by a few tens of micrometers. The measured ratio is not influenced by this increase in current.

Finally the blank is measured again to monitor possible changes in the background of the measurement.

The weighted mean of the three measurements gives the final ^{10}Be/^{9}Be ratio of the sample. Samples with a ^{10}Be/^{9}Be ratio of 10^{-9} can be measured to a precision of about 3%. Counting statistics are the limiting factor in the uncertainty and in the limited amount of data available at present no external error is observed. With a Cs^+ current of 600 nA the $^{16}O^{5+}$ current is typically 200–300 pA with a yield of secondary BeO^- ions of about 1%. The analysis time mentioned above (30 min elapsed time) does not use up all the sample. This time can be extended up to 1.5 h, which would make the measurement of ^{10}Be/^{9}Be ratios in the 10^{-10} range, to a precision of around 10 %, possible. Background ratios are $\sim 5 \times 10^{-11}$.

4. Results of first test measurements

As a preliminary test of the method two samples (CM16 and CM17) were taken from the

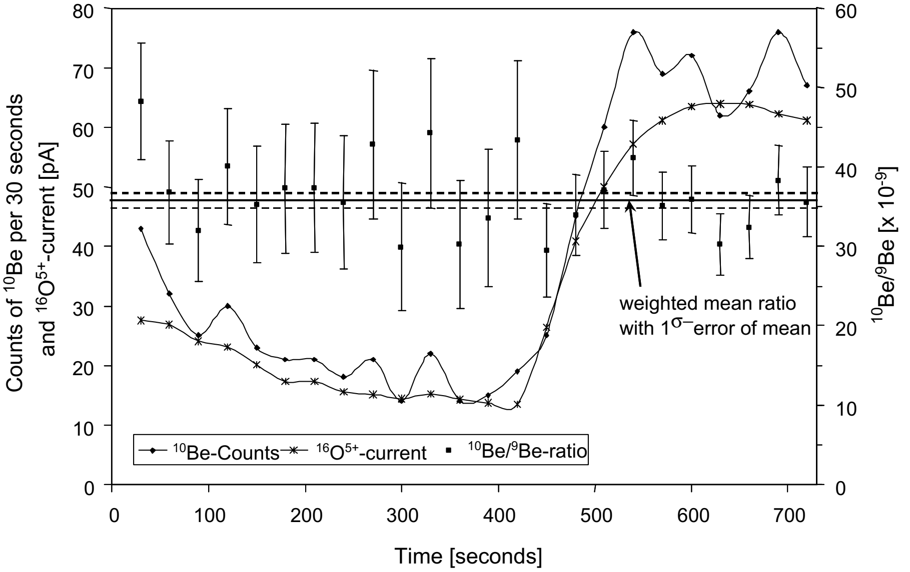

Fig. 3. Typical run of a sample showing the ^{10}Be count rate and the ^{16}O^{5+} current as well as the resulting ^{10}Be/^{9}Be ratio as a function of time. For technical reasons the Cs^{+} current curing this measurement was about 100 nA.

D11–1 ferromanganese crust. The ^{10}Be/^{9}Be ratios at various depths in the crust have previously been measured on the ISOLAB-120 SIMS instrument in Oxford [3]. Fig. 4 shows the results of the ISOLAB-120 measurements connected with straight lines together with the ratios of the two test samples measured with Accelerator SIMS. The horizontal bars through the data points indicate the depth range out of which the corresponding sample was taken. The vertical error bars represent the 1 σ-error of the ^{10}Be/^{9}Be ratio of the sample, which in the case of the ISOLAB-120 measurements is counting statistics convoluted with an empirically determined external error. A possible external error in the Accelerator SIMS measurements is too small to be quantified with the amount of data available at the moment. The error of 3% in the nominal value of the M3 standard was not included into the errors.

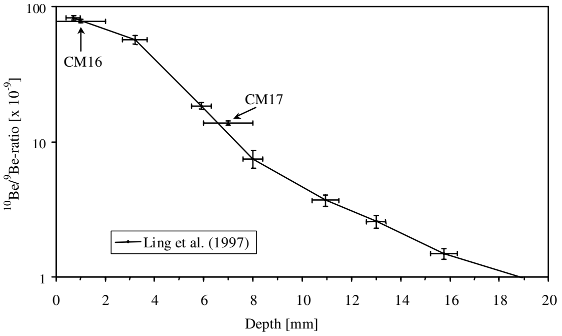

Fig. 4. ^{10}Be/^{9}Be ratio as a function of depth in ferromanganese crust D11–1 comparing the two samples measured with Accelerator SIMS with data published by Ling et al. [3].

Belshaw et al. [9] report a discrepancy between the published ratio of the M3 standard and the ratio measured with the ISOLAB-120 when calibrating to the NIST SRM-951 boron standard. To take this into account the ratios measured with Accelerator SIMS were normalised to the ratio of the M3 standard measured with the ISOLAB-120 (3.09×10^{-8}) [9, Table 1].

As can be seen from Fig. 4, the Accelerator SIMS measurements fit the previously measured data very well and the precision of the Accelerator SIMS measurements is generally higher than that of the ISOLAB-120 measurements. The large sampling range is only due to the fact that CM16 and CM17 were regarded as test samples. Thus, taking greater care while sampling the crust would result in a higher depth resolution.

5. Conclusions

First measurements of natural ^{10}Be/^{9}Be ratios with AMS have been performed successfully and the analysed total sample sizes of about 100 ng of Be represent a unique achievement in the field of AMS. The test samples were measured to a higher precision than with ISOLAB-120 SIMS. It is also to be expected that the new Accelerator SIMS method will be more precise than the combination of conventional ^{10}Be AMS with ^{9}Be ICP-MS because the uncertainty in the conventional ^{10}Be AMS measurement alone is about the same size as in the Accelerator SIMS measurement. However, a detailed comparison of the new Accelerator SIMS method to the already existing methods is necessary before it can be routinely used.

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