

Carrier free $^{10}\text{Be}/^9\text{Be}$ measurements with low-energy AMS: Determination of sedimentation rates in the Arctic Ocean

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[5]. Average sedimentation rates of 0.27 cm/kyr (09JPC) and 0.23 cm/kyr (14JPC) had been calculated based on the decrease of $^{10}\text{Be}/^{9}\text{Be}$ in the core. With the new ^{10}Be half-life of 1.387 Myr [8,9] these values change to 0.29 cm/kyr (09JPC) and 0.25 cm/kyr (14JPC), respectively.

From each core (09JPC, 14JPC) two samples were chosen to be remeasured with the carrier-free method. This serves also as an additional test of the new method in comparison with a conventional determination of the $^{10}\text{Be}/^{9}\text{Be}$ ratio using a combination of AMS and ICP-MS.

2.2. Sample preparation

The procedure of leaching the seawater-derived isotopic signature of Be from a marine sediment sample for carrier-free $^{10}\text{Be}/^{9}\text{Be}$ measurements is adapted from [10]. About 1 g of sediment is first leached in 40 ml acetate buffer (pH 4.66) for 2 h to dissolve the carbonate fraction. After centrifugation and removal of the supernatant the Be fraction is extracted from the sample in a second leaching: During another 2 h of shaking, the seawater-derived ferromanganese coatings are dissolved in 40 ml of 0.05 M hydroxylamine hydrochloride in 15% acetic acid, buffered to pH 4 with NaOH. After centrifugation the supernatant is evaporated and redissolved in ca. 5 ml 6 M HCl. The Fe is separated on a column containing 2 ml BioRad AG1x8 (100–200 mesh). The resin is first rinsed with 10 ml MilliQ water, cleaned with 10 ml 0.3 M HCl and conditioned with 6 ml 6 M HCl. The sample is then loaded onto the column and the Be fraction is collected immediately, the column is further rinsed with another 5 ml 6 M HCl, which are also collected and combined with the Be fraction for further processing.

Afterwards, the material is evaporated and redissolved in ca. 10 ml 0.4 M oxalic acid. Ca in the material may be precipitated in this step. If this is the case, after a centrifugation the supernatant is again evaporated and redissolved in 5–15 ml oxalic acid, else the original solution is processed.

The next purification step is carried out on 1 ml columns of BioRad AG50x8 (200–400 mesh) [11]. The resin is cleaned with 6 ml 5 M HNO_3 and rinsed with 8 ml MilliQ water. Further, the resin is conditioned with 8 ml 0.4 M oxalic acid. The sample is loaded in a volume of 5–15 ml of the same solution. 15 ml of this solution are used to wash the sample down and to remove cations like Fe, Al and Ti. After rinsing with MilliQ water, 6 ml of 0.5 M HNO_3 are used to elute Na. Finally, the Be fraction is collected in 12 ml 1 M HNO_3 .

This step is followed by a coprecipitation with 0.5–1 mg Fe, which is cleaned in advance using a BioRad AG1x8 column to avoid any introduction of ^9Be in this step. The sample is dried at 80 °C and afterwards oxidized at 650 °C in a crucible for 1–2 h. After mixing with ca. 4 mg Nb powder (325 mesh) the material is pressed into a cleaned Ti cathode-holder.

For the treatment of sediment samples the hydroxylammonium chloride, acetic acid and sodium hydroxide have pro analysi purity, all other chemicals are used at suprapure level.

2.3. Ion source

The carrier-free Be samples are analyzed at the compact TANDY AMS system, which originally had been designed for ^{14}C measurements at low energies [12]. In the meantime, the setup has been modified: By installing a second magnet on the high-energy (HE) side of the spectrometer the background level for $^{10}\text{Be}/^{9}\text{Be}$ measurements has been reduced below 10^{-15} [13]. The $^{10}\text{Be}/^{9}\text{Be}$ sample ratios are normalized against the in-house standard S1 with a nominal $^{10}\text{Be}/^{9}\text{Be}$ ratio of 9.51×10^{-8} . This value is corrected for the new ^{10}Be half-life [8,9] according to [14].

The separation of the ^{10}B interference from ^{10}Be is achieved by the degrader foil method in the setup described in [13]. When selecting the 1+ charge state after the accelerator and the 2+ charge state after the degrader foil the overall transmission from the low energy side to the detector reaches up to 10%. The stability of the setup within a run is illustrated by the results of our standard S1 during three beam times (Fig. 1). Different tunings and slit settings may be required for appropriate ^{10}B suppression and lead to different values for the standards between the runs.

Typical carrier-free samples prepared from 1 g marine sediment show $^{10}\text{Be}/^{9}\text{Be}$ ratios above 10^{-9} and develop currents of 0.5–1 nA. Samples are measured for ca. 600 s and give 10–30 ^{10}Be counts per second. The determination of the $^{10}\text{Be}/^{9}\text{Be}$ ratio is more sensitive to background from stable ^9Be than it is to contamination with ^{10}Be . Therefore, special attention is turned to the preparation of the samples and the measurement of the low currents.

Currents even below 100 pA can be measured reliably in the new setup. The blank level of the current is checked in several ways: Blanks containing only Nb powder are measured to control any cross contamination during the pressing of the sample material into the sputter targets. The Nb blanks usually show only few pA on the HE side. Fully processed blanks are produced starting from the leaching substance and by treating these blanks in the same way and with the same amount of chemicals as used for the normal samples. Thereby, input of ^9Be or ^{10}Be by the chemicals used for the processing and cross contamination during sample preparation and in the ion source can be monitored. These blanks typically show ^9Be HE currents of 10–15 pA and ^{10}Be rates of less than 2 counts per minute, which corresponds to $^{10}\text{Be}/^{9}\text{Be}$ ratios of $1\text{--}2 \times 10^{-9}$. Further, targets of the S1 standard with varying Be content are measured to determine a potential current dependence of the $^{10}\text{Be}/^{9}\text{Be}$ ratio. A correction for such a dependence may require an HE current offset of up to 15 pA. Usually, this offset correction on the current already explains the currents of the Nb press blanks and in some cases it is even larger than the current of the

3. Results

3.1. Results of the $^{10}\text{Be}/^9\text{Be}$ ratio measurements

From the three ODP sediment samples used in this study the Be content was extracted in several independent preparations (A, B, C in Fig. 2). The three samples show $^{10}\text{Be}/^9\text{Be}$ ratios in the 10^{-8} range and are characterized by different shapes and colors of the symbols in Fig. 2. The differences in the measurement settings and the chemistry yields are illustrated by the varying currents.

All the results for the $^{10}\text{Be}/^9\text{Be}$ ratios are consistent for the individual samples. Uncertainties of the single measurements include measurement stability, counting rate, blank correction and the uncertainty of the standard. The overall internal 1σ uncertainty of a measurement on a single target typically is 2–5%. The mean

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