

Full Length Article

A simple method of purifying authigenic ^{10}Be from sediments for AMS-analysisJulia Loftfield^{a,*}, Johannes Lachner^b, Maylin Malter^a, Konstanze Stübner^b, Florian Adolphi^a^a Alfred Wegener Institute, Helmholtz Centre for Polar and Marine Research, Am Handelshafen 12, 27570 Bremerhaven, Germany^b Helmholtz-Zentrum Dresden-Rossendorf, Bautzner Landstr. 400, 01328 Dresden, Germany

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ABSTRACT

The cosmogenic radionuclide ^{10}Be is used for a variety of applications, its analysis however requires laborious purification methods. We developed a simple purification protocol for Be from sediment samples that works without strongly hazardous chemicals or time consuming and expensive ion exchange columns. The combination of hydroxide precipitations and precipitation in NaHCO_3 was compared to an established protocol of hydroxide precipitations and ion exchange columns. The new method has a slightly lower Be-yield and purity of the resulting samples. However, this does not have a significant influence on performance during AMS-measurement where both methods performed equally well. The avoidance of column chromatography reduces sample preparation costs and space requirements in the lab allowing for more samples to be prepared simultaneously.

1. Introduction

As a cosmogenic radionuclide with a relatively long half-life of 1.387 ± 0.012 Ma [8,20], ^{10}Be is used in a variety of applications such as reconstructions of solar activity [33] and geomagnetic field intensity [24], exposure dating [2], determining the rates of sedimentation [30], denudation [35], as well as soil formation and weathering [11]. Furthermore, the ages of marine sediments can be determined by decay of ^{10}Be (e.g. Frank et al. [13]). It has also been used for synchronizing timescales of different climate archives [1] or infer information about carbon cycle changes in the past [19,25]. Some of these applications require high-resolution time series of ^{10}Be -measurements and thus, many samples. For these applications, developing a purification protocol that is fast, reproducible and yields sufficiently pure Be-samples with a high Be-yield is essential. In addition, beyond the requirements of the particular application an alternative methodology might suite some users better from practical perspective and thus, contribute to the expansion of the technique.

In order to measure ^{10}Be from environmental samples by AMS it is necessary to first dissolve or leach the samples and purify them afterwards. Purification is necessary as the sample matrix (e.g. Ca, Fe, Si, Mn, Al, P, Ti) can inhibit ionization of the sample in the ion source. Purification is also needed to reduce the concentration of boron in the sample – the isobar of ^{10}Be . Several methods for extraction of Be from sediments

and rocks and purifying it afterwards exist. Some purification methods are time consuming or involve hazardous chemicals (e.g. [34]). Here, we offer a low-cost alternative that might be more suitable for some researchers' applications or practical considerations.

Preparing ice samples for ^{10}Be measurements can nowadays be reduced to very few steps (e.g. [26]), sediment and rock samples however require more preparation as they contain much higher concentrations of matrix elements that might interfere in the ionization in the AMS and dilute the BeO. Furthermore, samples need to mimic the standards used for normalization in the AMS-measurement. For this purpose, Be is often purified by a combination of hydroxide precipitations and ion exchange chromatography [18,31]: The hydroxides of the alkaline and alkaline earth metals – with the exception of $\text{Be}(\text{OH})_2$ – dissociate completely in solution. Therefore, Na, K, Ca and Mg are readily separated from Be through a hydroxide precipitation at pH 8 – 9. Other common matrix elements can be separated by anion (e.g. Fe, Mn) or cation (Al, B, Ti) exchange chromatography. Alternatively, Be can also selectively be extracted from the sample solution: Bourlès et al. [5] and Ménabréaz et al. [22] use organic solvents to extract Be as Be acetylacetonate; Stone [34] fuses the samples with KHF_2 and NaSO_4 , thereby producing BeF_4^{2-} which is then extracted with hot water, while the insoluble fluorides of Al, Fe and Ti remain solid, thereby combining dissolution of the sample and purification of Be into one single step. An overview of methods is given by Stone [34].

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All of these methods are either time consuming and expensive, or involve organic solvents or hazardous chemicals.

The aim of this paper is to present a simple purification protocol that does neither involve strongly hazardous chemicals nor time consuming and expensive ion exchange columns and allows a high sample throughput. We developed and tested the protocol for meteoric ¹⁰Be in the authigenic Fe-Mn-oxihydroxide phases in marine sediments obtained by chemical leaching. In principle, this protocol is also suitable for in-situ ¹⁰Be applications in quartz samples if Si is removed prior to purification, e.g. by fuming with HF. We compare this method (from now on called “precipitation protocol”) to an ion-chromatography-based method (from now on called “ion exchange chromatography”) with

respect to yield, purity, and performance in the AMS of the prepared samples, as well as sample preparation time and throughput.

2. Material & methods

An overview of the applied leaching and purification methods is given in Fig. 1 and Fig. S1.

Two different sediment core samples were chosen for purification. The first sample, PS115/2-28-3 – 85 cm depth, was taken during FS Polarstern cruise 115/2 in 2018 with a Kasten corer on the Lomonosov Ridge (82.8 °N, 142.5 °E) at a water depth of 1247 m [32]. It consists of brown, silty clay [32] and has a low CaCO₃-content of 1 % (unpublished

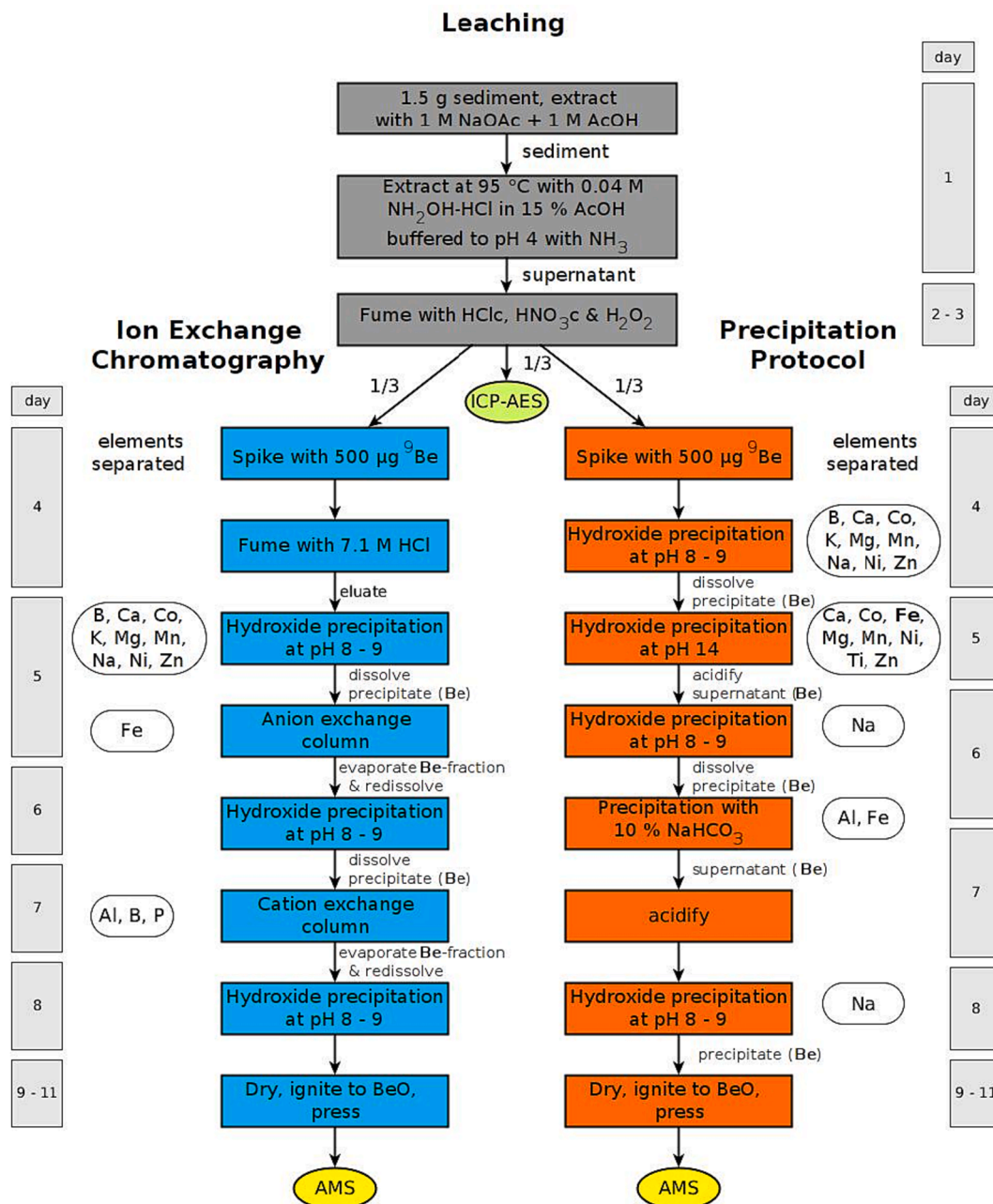


Fig. 1. Leaching and purification steps. Rectangles: leaching steps (top center / gray), purification steps with hydroxide precipitations and column chromatography (left / light blue) & purification steps with hydroxide precipitations and precipitation with NaHCO₃ (right / red-orange). White ovals: relevant elements separated at individual purification steps. Ovals: measurements with AMS (yellow) and ICP-AES (green). Light gray bars: approximate time needed for leaching / purification procedures A more detailed description is given in Fig. S1, including additional steps and aliquots that were introduced for evaluation purposes as well as steps that proved to be superfluous.

data R. Stein & O. M. Benson). This sample is referred to as “low Ca” sample.

The second sample (referred to as “high Ca”), PS1241-2 (2 – 7 cm depth), was taken with a giant box corer during FS Polarsten cruise ARK-II/5 in 1984 from the Norwegian Sea (68.3 °N, 3.7° E) at a water depth of 1890 m [4]. It is made up of light grayish-brown silty clay with some fine sand and abundant benthic foraminifera (unpublished shipboard document). Due to the foraminifera it has a high CaCO₃ content of 56.7 % [16].

The samples were freeze dried and homogenized. Three samples of ~ 1.5 g sediment each were taken from both cores and leached separately. The samples were then split into three aliquots, two of the aliquots were processed by the ion exchange and the newly developed precipitation protocols respectively, and the third aliquot was used for chemical characterization by ICP-AES (see Fig. 1).

2.1. Leaching

We leached the authigenic fraction of the sediments based on Gutjahr et al. [14] with some modifications (see Fig. 1, top center): 1.5 g of sediment were leached with a mixture of 1 M NaOAc and 1 M AcOH (52:48) at room temperature for 2 h and under constant stirring with a magnetic stirrer. The suspension was centrifuged and the supernatant – the carbonate fraction – was disposed. The sediment was further leached with 0.04 M NH₂OH-HCl in 15 % AcOH buffered with NH₃ to pH 4 at 95 °C for 4 h under constant stirring. All pH values were adjusted using indicator papers. Samples were again centrifuged and the supernatant collected in a Teflon beaker, evaporated to near dryness and for oxidation re-dissolved in 2 mL aqua regia and 1 mL H₂O₂. The solution was allowed to react for 1 h and was then evaporated to near dryness. The residue was again dissolved in 2 mL H₂O₂, 9 mL HClc added and let react for 10 min. 3 mL HNO₃c were added and the solution let react for > 4 h on a hotplate (120 °C) and afterwards evaporated (after Henkel et al. [15]).

The leaching of the exchangeable fraction (see Gutjahr et al. [14]) was omitted as it was found to contain less than 1 % of the total Be in agreement with earlier studies [36].

The residue was dissolved in 45 mL 1 M HCl. We split the dissolved samples by volume into three aliquots of 15 mL and weighed the aliquots. One part was measured with ICP-AES and the other two parts transferred to Teflon beakers (“ion exchange chromatography”) and 50 mL centrifuge tubes (“precipitation protocol”). The latter two aliquots were then spiked with 0.5 mL ⁹Be-carrier (1000 mg/L, LGC 998969–73 – ¹⁰Be/⁹Be-ratio of (3.74 ± 0.30) * 10⁻¹⁵, tested in Merchel et al. [23]) each (see Fig. 1).

2.1.1. ICP-AES-measurement

For ICP-AES analysis the 15 mL aliquot was dried, re-dissolved in 5 mL 1.5 M HNO₃, split into 5 aliquots of 0.98 mL and 2.2 mL of 1.5 M HNO₃ added to each aliquot. 3 of the aliquots were then spiked with 0.02 mL Be standard solution (4 mg/L diluted from Scharlab 21078301, 1000 mg/L; see Table 1). Samples were measured via ICP-AES (Thermo Fisher Scientific Inc., ICP-OES-iCAP7400) using an internal yttrium standard. ⁹Be concentrations were calculated using standard addition

Table 1

Aliquot volumes, added HNO₃ and Be-spike for ICP-AES-measurement. Each sample was split into 5 equal aliquots, 3 of which were spiked with ⁹Be-standard (4 mg/L) and ⁹Be-concentrations calculated using standard addition.

Aliquot #	Sample [mL]	1.5 M HNO ₃ [mL]	⁹ Be-spike [mL]	⁹ Be added [μg/L]
1	0.98	2.2	0	0
2	0.98	2.2	0	0
3	0.98	2.2	0.02	25
4	0.98	2.2	0.02	25
5	0.98	2.2	0.02	25

following Ellison & Thompson [12] and Kelly et al. [17]. Apart from Be we also measured Al, B, Ca, Co, Fe, K, Mn, Ni, P, Si, Ti, V and Zn via ICP-AES but without standard addition.

2.2. Ion chromatography and hydroxide precipitation (“ion exchange chromatography”)

The purification was based on Simon et al. [31] and is hereafter described in detail.

2.2.1. Step 1: Fuming with HCl

For the “ion exchange chromatography” protocol (Fig. 1, left side) the sample aliquots were dried and 10 drops of HCl (7.1 M) added and evaporated to near dryness twice. The samples were rinsed into a 15 mL centrifuge tube and purified according to the method shown in Fig. 1, left side.

2.2.2. Step 2: First hydroxide precipitation

Beryllium is precipitated as Be(OH)₂ by adding ca. 1 mL NH₃(aq) (28 %) dropwise to the solution until pH 8 – 9 was reached. A reaction time of 30 min was allowed (if reaction continues longer manganese oxides will precipitate with beryllium hydroxides). Samples were centrifuged (5 min at 4500 rpm), decanted, and washed twice with strongly diluted NH₃(aq) (pH 8 – 9, centrifuged 10 min at 4500 rpm). The supernatant and wash were collected, purification continued with the precipitate, which contains the Be.

2.2.3. Step 3: Anion exchange column

We dissolved the samples in 1 mL HClc and pipetted them onto a column filled with 15 mL of anion-exchange resin (Dowex® 1 x 8, 100–200 mesh, rinsed with 30 mL Milli-Q (MQ) water and conditioned with 30 mL 10.2 M HCl). The Be fraction was eluted with 32 mL 10.2 M HCl and collected in a Teflon beaker.

Afterwards we evaporated the samples until near dryness, dissolved them in 7.1 M HCl and transferred them to 15 mL centrifuge tubes.

2.2.4. Step 4: Second hydroxide precipitation

Beryllium is again precipitated as Be(OH)₂ at pH 8 – 9 as in step 2.

2.2.5. Step 5: Cation exchange column

We dissolved the samples in 1.5 mL 1 M HCl and pipetted them onto a column filled with 10 mL of cation-exchange resin (Dowex® 50 x 8, 100–200 mesh, rinsed with 20 mL MQ water and conditioned with 20 mL 1 M HCl). The Boron fraction was eluted with 28.5 mL 1 M HCl and discarded. Afterwards we eluted the Be fraction with 90 mL 1 M HCl and collected it in a Teflon beaker. We evaporated the samples until near dryness, dissolved them in 7.1 M HCl and transferred them to 15 mL centrifuge tubes.

2.2.6. Step 6: Third hydroxide precipitation

The third hydroxide precipitation was carried out as the first (see step 2) and second. The reaction was allowed to continue over night. Drying and ignition of the samples is described in section 2.4.

At each hydroxide precipitation step the supernatants (including the wash) were collected, evaporated to dryness, re-dissolved in 20 mL 1.5 M HNO₃ and measured with ICP-AES (IEC1, IEC3 and IEC5 in Fig. S1). After both ion exchange columns, aliquots were taken and also measured with ICP-AES (IEC2 and IEC4 in Fig. S1). Volumes of aliquots and dilutions for ICP-AES-measurements are given in Table S1.

2.3. Hydroxide precipitations and precipitation in NaHCO₃ (“precipitation protocol”)

The “precipitation protocol” is shown in Fig. 1, right side. While most elements that form basic hydroxides can easily be separated from Be via hydroxide precipitation at pH 8 – 9, others like Fe and elements forming

amphoteric hydroxides like Al will co-precipitate and need further purification steps. We used the fact that Be forms amphoteric hydroxides and is hence soluble at pH 14 [27], while the basic hydroxides of iron and other elements precipitate at pH 14. The separation of Al from the samples is then achieved by applying the method of Parsons & Barnes [28], improved by Britton [6]. This “method is based on the total insolubility of aluminum and ferric hydroxide in a 10 per cent. boiling acid sodium carbonate solution and on the total solubility of beryllium hydroxide in the same” [28]. Since our samples contain much lower Be-concentrations, it was sufficient to precipitate the Al-hydroxide at room temperature.

2.3.1. Step 1: First Hydroxide precipitation at pH 8 – 9

Beryllium is precipitated as $\text{Be}(\text{OH})_2$ at pH 8 – 9, while B, Ca, K, Mg, Mn and Na stay in solution.

After leaching the sample is present in 15 mL 1 M HCl in a 50 mL centrifuge tube. The hydroxide precipitation was performed as in step 2 of “ion exchange chromatography”. The supernatant and wash solution were combined (~20 mL), evaporated, dissolved in 1.5 M HNO_3 and analyzed by ICP-AES (Fig. S1, P1). The precipitate, which includes $\text{Be}(\text{OH})_2$, was further purified.

2.3.2. Step 2: Hydroxide precipitation at pH 14

We performed another hydroxide precipitation – at pH 14 – to remove Fe and Ti and further reduce Ca, Mg, Mn, and Ni. Be and Al stay in solution, while Fe, Ti and the other elements precipitate.

The precipitate from step 1 was dissolved in 1 mL HNO_3 and NaOH pellets were carefully added until pH 14 was reached. Samples were allowed to react for 18 h (overnight), centrifuged (10 min at 4500 rpm), decanted into 15 mL centrifuge tubes, and the precipitate was washed once with freshly prepared 6.5 M NaOH. The supernatant and the washing liquid, which contains Be, were combined and further purified; the precipitate was dissolved in 1.5 M HNO_3 , weighed and analyzed by ICP-AES (Fig. S1, P2).

2.3.3. Step 3: Second Hydroxide precipitation at pH 8 – 9

A second hydroxide precipitation at pH 8 – 9 was performed to remove the Na introduced in step 2.

We acidified the solute of step 2 by adding drops of HCl (~3 mL) and conducted a second hydroxide precipitation at pH 8 – 9 by adding $\text{NH}_3(\text{aq})$ (28 %). After two hours the samples were centrifuged and washed twice with dilute $\text{NH}_3(\text{aq})$ (pH 8 – 9). We dissolved the precipitated hydroxides, which include $\text{Be}(\text{OH})_2$, in 2 mL dilute HNO_3 (2 %). The solution was weighed and an aliquot was taken for measurement at ICP-AES (Fig. S1, P3).

2.3.4. Step 4: Fuming

This step was introduced as we initially had precipitates forming from the samples after full purification. In subsequent experiments we determined that these precipitates were likely over-saturated silicates that re-dissolve upon addition of more liquid. These did neither affect the performance of the samples in the AMS nor the $^{10}\text{Be}/^9\text{Be}$ ratios. Hence, this step can be omitted.

Samples were transferred to Teflon beakers and evaporated on a hotplate. Twice we added 1 mL of HNO_3 and 0.5 mL HCl (7.1 M) to the samples and evaporated the samples to dryness. We dissolved the samples in 0.5 mL dilute HNO_3 (2 %), transferred them to 15 mL centrifuge tubes, and rinsed the beakers three times with 0.5 mL HNO_3 (2 %), adding the rinsing solution to the solute (total of 2 mL). Samples were weighed and an aliquot was taken, diluted with 1.5 M HNO_3 and analyzed with ICP-AES (Fig. S1, P4).

2.3.5. Step 5: Precipitation with NaHCO_3

With this step we remove Al and part of the remaining Fe. Beryllium stays in solution, while Al and Fe precipitate.

We brought the sample to pH 5 – 6 by adding NH_3 , avoiding

precipitation of $\text{Be}(\text{OH})_2$ at higher pH. Then, 5 mL of 10 % NaHCO_3 solution (saturated) were added. Samples were allowed to rest 8 h at room temperature under constant stirring. They were centrifuged for 20 min at 4500 rpm and the solute decanted. We did not rinse the precipitate as we found that this leads to re-dissolution of $\text{Al}(\text{OH})_3$ while increasing the Be-yield only marginally.

We dissolved the precipitate, which contains Al and Fe, in HCl (10 %) and performed a hydroxide precipitation as in step 3 in order to remove the added Na from the sample which affects the ionization in the ICP-AES. The resulting precipitate was dissolved in 1.5 M HNO_3 and analyzed with ICP-AES (Fig. S1, P6).

Purification continued with the Be containing supernatant.

2.3.6. Step 6: Degassing of CO_2

In order to remove the carbonate ions, we dropwise added concentrated HCl to the supernatant of step 5 leading to degassing of CO_2 . The centrifuge tubes were placed in a sand bath at 120 °C, and reaction was allowed to continue until no formation of bubbles was visible (≥ 2 h). This may also be performed at room temperature if the duration is increased.

2.3.7. Step 7: Third Hydroxide precipitation at pH 8 – 9

A 3rd hydroxide precipitation at pH 8 – 9 is needed to separate Be from the Na-rich matrix. Beryllium is once more precipitated as $\text{Be}(\text{OH})_2$.

The hydroxide precipitation at pH 8 – 9 was conducted as in step 3 (apart from the acidification) but the precipitate, which contains $\text{Be}(\text{OH})_2$, was rinsed three times with MQ water instead of $\text{NH}_3(\text{aq})$. This is done in order to avoid the formation of NH_4Cl during the drying process.

As we wanted to take an ICP-AES aliquot reflecting the purity of the final sample, we took an aliquot of the previous precipitate. Since it is difficult to take a precisely defined aliquot from the precipitate, we dissolved it in 5 mL HCl (10 %), weighed it and took a 0.5 mL aliquot. This was evaporated to dryness and dissolved in 5 mL 1.5 M HNO_3 for ICP-AES analysis (Fig. S1, P5). With the rest of the precipitate we continued as described above. This re-dissolution and pH 8 – 9 precipitation were only needed in order to take an ICP-AES aliquot and is not required during normal sample preparation (see Fig. 1).

2.4. Drying, ignition & pressing

For AMS-analysis the samples need to be calcined to BeO_2 , mixed with Nb, and pressed into Cu-cathodes.

We transferred the final hydroxide precipitates of both purification methods into quartz crucibles using disposable pasteur pipettes. The pipette and the tubes were rinsed 2 – 3 times with 1 – 2 drops of MQ water and the rinsing water was added to the quartz vial. Samples were dried overnight on a hotplate at 80 °C. The crucibles were covered with lids and calcined in a muffle oven for 2 h at 900 °C. After cooling, we weighed the samples and added Nb in a ratio 1:4 w/w ($\text{BeO}:\text{Nb}$). We homogenized the samples and pressed them into copper cathodes. AMS-measurements were performed at DREAMS [21,29]. All measurements were done relative to the standard “SMD-Be-12” with a weighted mean value of $(1.704 \pm 0.030) \cdot 10^{-12}$ [3].

2.5. Chemicals and lab requirements

The employed chemicals were all of pro analysi purity (p. a.) apart from HCl and HNO_3 which were distilled from p. a., $\text{NH}_2\text{OH}\cdot\text{HCl}$ (99+% pure) and NaOAc (99 % pure).

Minimum lab requirements and equipment for the precipitation protocol are: fume hood, magnetic stirrer or sample shaker, centrifuge, heating plate and muffle furnace. A sand bath or heating block are optional for the degassing of CO_2 (step 6).

3. Results

Table 2 and Fig. 2 show the sample compositions after leaching (top) and after purification with the two protocols (bottom). Even though leachates of the two samples are of very different elemental composition, mainly regarding the content of Ca, Fe and Mn (top row: “Leachate”), the purification methods are equally efficient. The ion exchange chromatography method efficiently removed almost all other elements apart from Be. The remaining Ca and Fe concentrations correspond to the process blank. The precipitation protocol was not as efficient. 3 – 6 % of Fe, 4 – 17 % of Al and almost all P (80 – 100 %) was still present after purification as the protocol does not include any method that segregates P from Be. However, this method is more efficient at removing Ca, Ti and Mn from the sample. In any case, as discussed below, these remaining impurities did not affect the AMS-measurement. Concentrations of Al, Be Fe, Ti, Ca, and Mn are presented in Table 2; masses of all elements at different steps of the purification procedures and after leaching are given in Table S2 & Table S3.

The obtained ⁹Be-currents of the prepared targets in the AMS are pictured in Fig. 3. Each sample was measured 4 times until a statistical uncertainty below 1.7 % – the uncertainty of the nominal value of the standard – was achieved.

Table 3 shows the authigenic ⁹Be contents of the sediment leachate (“L0” – measured with ICP-AES), the ¹⁰Be/⁹Be ratio of the AMS-measurements, the resulting ¹⁰Be-concentration in the sediment as well as the authigenic ¹⁰Be/⁹Be ratio of the samples.

4. Discussions

4.1. Be yield and purity of samples

The Be yield of the precipitation protocol of about 90 % is not as high as that of the ion exchange chromatography method but still high enough to supply sufficient material for a measurement, where we saw no noticeable difference in Be-currents between the two methods (see 4.2 AMS performance). However, we note that the yield of the IEC

protocol is likely slightly overestimated as it was determined before the final pH 8 – 9 precipitation.

During precipitation at pH 8 – 9 about 1 – 2 % Be is lost, and the precipitation at pH 14 leads to a loss of about 2 %. Beryllium may co-precipitate with iron hydroxide at pH 14, or may not have enough time to react thoroughly at pH 8 – 9 to form insoluble Be(OH)₂. It is therefore important to thoroughly wash the precipitates at pH 14 to ensure that no Be is “trapped” in the precipitate and to allow for enough reaction time at pH 8 – 9. The first hydroxide precipitation is set to ½ h to separate Mn which precipitates with a delay to Be. A full separation of Mn and Be is achieved at pH 14.

After fuming the samples with HNO₃ and HCl (see Fig. S1) about 5 % of Be cannot be accounted for. This is probably due to incomplete re-dissolution of the samples and / or spattering while drying. This step may be omitted (see step 4).

When precipitating with NaHCO₃ further Be is lost. About 2 % is occluded by and carried down with the aluminum hydroxide (see Britton [6] and Parsons & Barnes [28]) another 2 – 3 % cannot be accounted for and is likely adsorbed to the walls of the centrifuge tube. Britton [6] states that washing the aluminum hydroxide precipitate with 10 % NaHCO₃ and combining the wash and the solute leads to a higher Be-yield. However, we found that this may also lead to a re-dissolution of Al(OH)₃ and therefore omitted that step.

Many of the elements that are separated from Be at pH 8 – 9 also precipitate at pH 14. Therefore it is conceivable that omitting the first precipitation at pH 8 – 9 would be a simplification of the procedure. When testing this, we found that this leads to a Be-loss of up to 40 %, likely due to co-precipitation with other hydroxides which are otherwise removed at pH 8 – 9. Similar losses were observed for Al, P and V. Hence, the initial precipitation of Be(OH)₂ at pH 8 – 9 cannot be omitted.

Furthermore, we found that the precipitation with NaHCO₃ works best when the salt load is low. Therefore, a second precipitation at pH 8 – 9 (with NH₃(aq)) is necessary before the precipitation with NaHCO₃. A final precipitation at pH 8 – 9 (with NH₃(aq)) removes the added Na and yields a Be(OH)₂ gel suitable for drying and ignition.

It may also be possible to use the Al-fraction for Al-analysis.

Table 2

Concentrations of selected elements directly after leaching (“L0”) after purification via ion exchange chromatography method (“IEC4”) and after precipitation protocol (“P5”) relative to the amount of sediment used. Concentrations after purification (“IEC4” & “P5”) also as percentage of added Be carrier or concentration after leaching (“L0”). IEC4 & P5 contain 500 µg Be carrier added to ~ 0.5 g sediment. Measurement uncertainties are 5 % for Be at L0 and 10 % for all other elements / measurements. Compare also Fig. 2.

Sample	Be			Al			Ca			Fe			Mn			Ti			
	L0	IEC4	P5	L0	IEC4	P5	L0	IEC4	P5	L0	IEC4	P5	L0	IEC4	P5	L0	IEC4	P5	
	[µg/g _{sed}]			[µg/g _{sed}]			[µg/g _{sed}]			[µg/g _{sed}]			[µg/g _{sed}]			[µg/g _{sed}]			
low Ca	I	0.145	1000	890	260	< 0.32	20	690	26	2.0	3900	19	140	3300	8.7	2.0	0.91	0.55	< 0.077
	II	0.141	1000	880	250	< 0.32	40	640	32	2.3	3600	19	150	3100	4.1	< 0.21	0.87	0.43	< 0.077
	III	0.141	1000	930	250	< 0.32	25	650	30	2.1	3600	20	130	3100	1.3	0.47	0.65	0.34	0.084
high Ca	I	0.140	1000	910	460	< 0.32	20	7400	27	20	2700	19	150	1300	2.7	0.86	2.3	1.5	0.19
	II	0.158	1000	880	460	< 0.32	20	7300	29	2.7	2600	20	120	1300	1.8	0.53	2.2	1.5	0.21
	III	0.155	1000	900	480	< 0.32	20	7600	26	1.8	2800	20	73	1400	2.0	< 0.21	2.4	1.3	0.14
Sample	IEC4		P5	IEC4		P5	IEC4		P5	IEC4		P5	IEC4		P5	IEC4		P5	
	% Be carrier			% L0			% L0			% L0			% L0			% L0			
low Ca	I	100	90	< 0.12	7.6	3.8	0.28	0.50	3.5	0.26	0.061	60	< 8.4						
	II	100	88	< 0.13	17	4.9	0.36	0.53	4.3	0.13	< 0.0069	49	< 8.9						
	III	100	92	< 0.13	10	4.6	0.32	0.53	3.6	0.043	0.02	53	13.0						
high Ca	I	100	91	< 0.069	4.3	0.36	0.26	0.72	5.7	0.21	0.07	63	8.1						
	II	100	88	< 0.069	4.3	0.40	0.036	0.75	4.6	0.14	0.04	67	9.7						
	III	100	90	< 0.067	4.2	0.34	0.02	0.71	2.6	0.14	< 0.015	54	5.9						

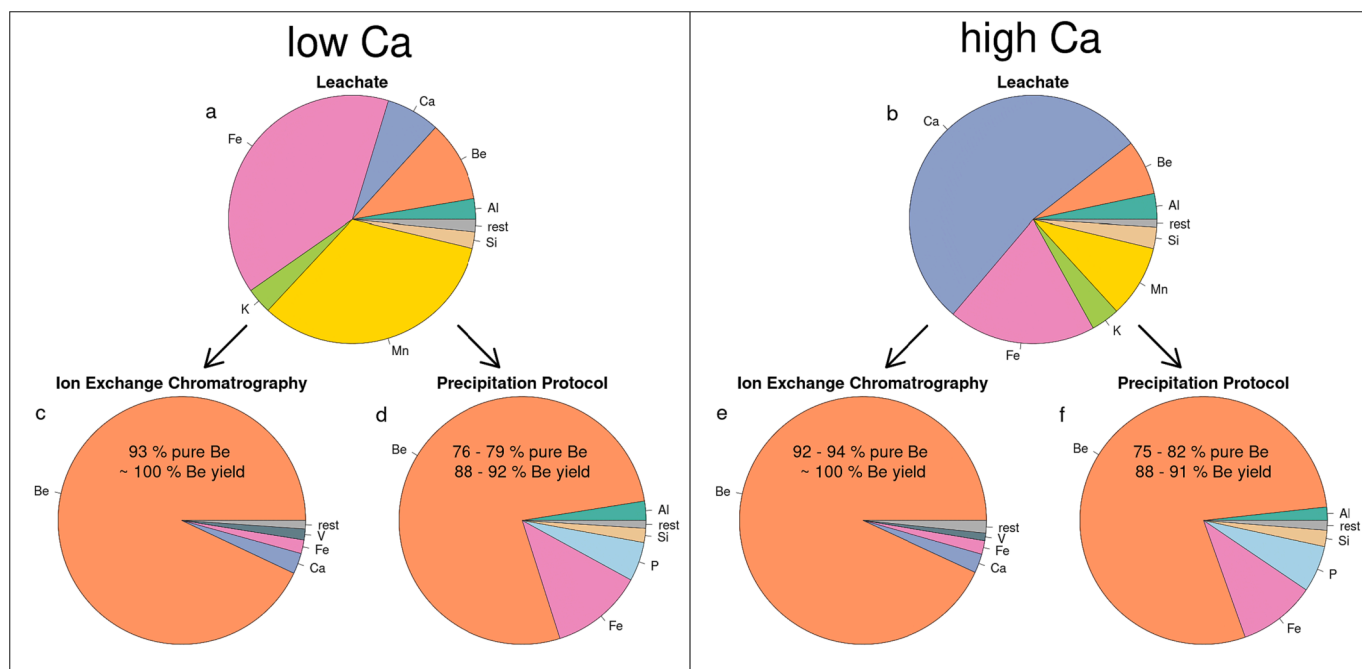


Fig. 2. Sample composition after leaching and purification. Upper row (a & b): sample composition after leaching (“L0”, see Fig. S1 for aliquot names) with 500 μg Be from a carrier added. Bottom row: sample composition after purification via ion exchange chromatography (“IEC4”, c & e) and after purification with the precipitation protocol (“P5”, d & f). The purity of extracted Be was 92 – 94 % (ion exchange chromatography, “IEC4”) and 75 – 82 % (precipitation protocol, “P5”). The Be-yield was ~ 100 % (ion exchange chromatography, “IEC4”) and 88 – 92 % (precipitation protocol, “P5”). See also Table 2.

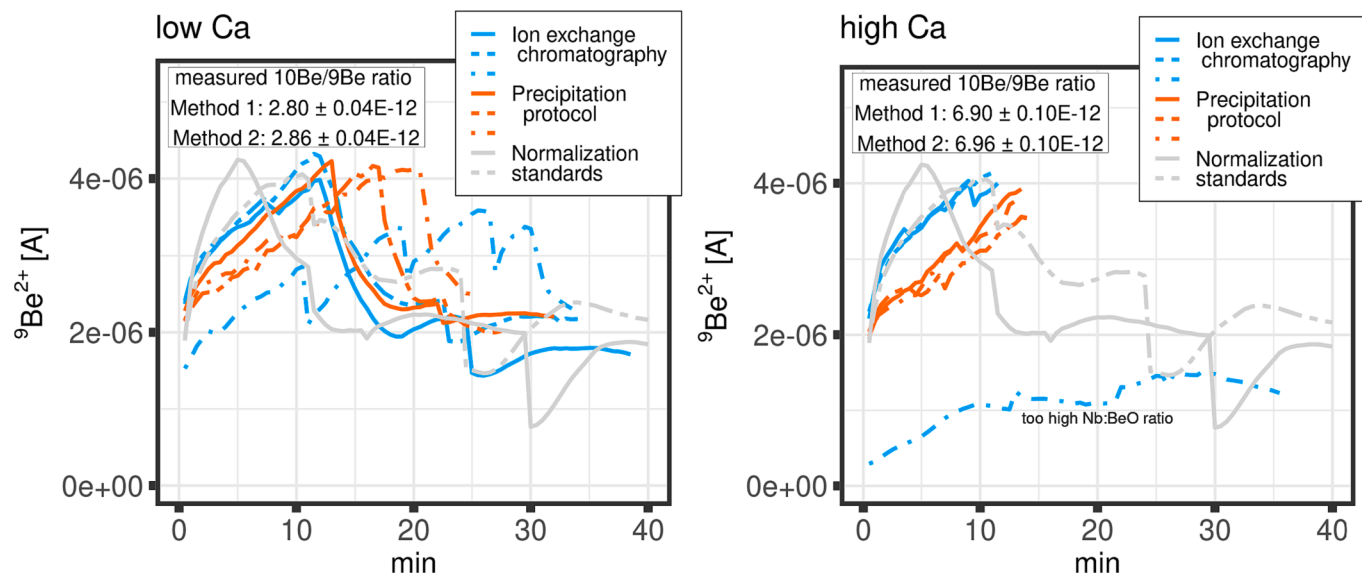


Fig. 3. AMS performance. AMS performance of targets created from “low Ca”-sample (left) and “high Ca”-sample (right) as indicated by the $^9\text{Be}^{2+}$ beam current of each sample over time. Blue lines represent samples purified with ion exchange chromatography, red lines samples purified with the precipitation protocol and gray lines the normalization standards. The plots of the normalization standards are cut off after 40 min. The third replicate of the “high Ca”-sample prepared via ion exchange chromatography had 2 ½ times the amount of Nb added as intended (blue dash-dotted line in right panel).

However, purity and yield of the Al-fraction were not measured during this project. Child et al. [7] remove Al by precipitating $\text{Be}(\text{OH})_2$ at pH 11.5 while dissolving $\text{Al}(\text{OH})_4^-$. When testing this, we found the separation not to be quantitative. As can be seen in Ochs & Ivy-Ochs [27], the pH-range for a successful separation is very narrow.

4.2. AMS performance

Both purification methods yield samples that are sufficiently pure so

that high and stable beam currents can be extracted in the AMS ion source. Samples from both methods required equally long sputtering time to achieve the desired statistical precision (see Fig. 3). In both sediment types the ^{10}B count rate in the detector was similar and below 100 events per second, so that the isobar did not affect the detection of ^{10}Be .

The samples prepared with ion exchange chromatography yield purer samples than the precipitation protocol samples. However, the yields are high (> 80 %) for both methods and thus no drastic

Table 3

^{10}Be - and ^9Be -data. ^9Be -values of ICP-AES-measurements, $^{10}\text{Be}/^9\text{Be}$ ratios of AMS-measurements, and resulting authigenic $^{10}\text{Be}/^9\text{Be}$ ratios for both protocols and all samples. The error weighted means of the authigenic $^{10}\text{Be}/^9\text{Be}$ ratio are estimated from averaging the authigenic ratios I, II and III. Reported uncertainties are ± 1 sigma.

		^9Be sed. conc. [10^{15} at/g] (AES - "LO")	$^{10}\text{Be}/^9\text{Be}$ AMS ratio [10^{-12} at/at]	^{10}Be sed. conc. [10^8 at/g] (AMS)	$^{10}\text{Be}/^9\text{Be}$ authigenic ratio [10^{-8} at/at]				
low	I	9.51 \pm 0.48	2.83 \pm 0.07	2.93 \pm 0.07	1.89 \pm 0.05	1.96 \pm 0.05	1.99 \pm 0.11	2.06 \pm 0.11	
	Ca	II	9.22 \pm 0.46	2.77 \pm 0.07	2.81 \pm 0.07	1.86 \pm 0.05	1.90 \pm 0.05	2.02 \pm 0.11	2.06 \pm 0.11
		III	9.22 \pm 0.74	2.80 \pm 0.07	2.86 \pm 0.07	1.88 \pm 0.05	1.93 \pm 0.05	2.04 \pm 0.17	2.09 \pm 0.17
	error weighted mean		9.34 \pm 0.32	2.80 \pm 0.04	2.86 \pm 0.04	1.88 \pm 0.03	1.93 \pm 0.03	2.01 \pm 0.07	2.06 \pm 0.07
high	I	9.19 \pm 0.46	6.76 \pm 0.16	6.88 \pm 0.17	4.54 \pm 0.11	4.62 \pm 0.11	4.95 \pm 0.28	5.04 \pm 0.28	
	Ca	II	10.30 \pm 0.51	7.08 \pm 0.17	6.97 \pm 0.17	4.63 \pm 0.11	4.70 \pm 0.11	4.62 \pm 0.26	4.56 \pm 0.25
		III	10.14 \pm 0.51	6.88 \pm 0.17	7.06 \pm 0.17	4.74 \pm 0.11	4.74 \pm 0.12	4.55 \pm 0.25	4.69 \pm 0.26
	error weighted mean		9.83 \pm 0.28	6.90 \pm 0.10	6.96 \pm 0.10	4.64 \pm 0.06	4.69 \pm 0.07	4.70 \pm 0.15	4.74 \pm 0.15

differences in the performance of the AMS targets can be expected. The prepared targets gave similar currents as standard targets which also behaved similarly over time, indicating that the sample purification does remove all contamination relevant to the AMS-measurement of these samples. Furthermore, it is reassuring to note, that adding too much Nb ("high Ca" sample III, ion exchange chromatography, see Fig. 3) does not affect the obtained measurement result in terms of ^{10}Be concentration and authigenic $^{10}\text{Be}/^9\text{Be}$ ratio for this sediment sample.

4.3. Lab routine / costs

Purification via the new protocol takes about 5 days after leaching before drying and ignition of the samples. It allows for 20 samples to be prepared simultaneously by a single person. The cost for consumables for purification via precipitation protocol adds up to about 2.5 € per sample compared to about 22 € via ion exchange columns (not taking into account drying, ignition and pressing of the targets). Note that the acids were distilled in house.

The procedure only requires standard lab equipment and chemicals. It does not involve hazardous chemicals (as Stone [34]), organic solvents (as Bourlès et al. [5] or Ménabréaz et al. [22]), or use up costly resins for the ion exchange columns (as Codilean et al. [9], Corbett et al. [10] or Kohl & Nishiizumi [18]).

5. Conclusion

The sample purification method we present here is suitable for purifying Be from sediments for AMS-measurement. Sediments prepared with this protocol performed as well during AMS-measurement as samples prepared via ion exchange chromatography method. The method only requires standard laboratory equipment and allows for 20 samples to be purified simultaneously. With this method it is possible to generate reliable Be data from sediment cores in a simple, low cost way, offering a viable alternative to the existing sample preparation methods. The presented method is scalable for larger sample batch size that in turn offers a potential avenue for higher sample throughput.

This protocol was developed for the efficient and low-cost preparation of marine sediment samples for meteoric ^{10}Be analysis, an application which often requires a large sample throughput. Although in principle applicable to all types of ^{10}Be samples, different cation loads are expected for different sample materials, and the proposed protocol may have to be adjusted and optimized for other applications.

CRediT authorship contribution statement

Julia Loftfield: Conceptualization, Methodology, Investigation, Formal analysis, Writing – original draft, Visualization. **Johannes Lachner:** Methodology, Formal analysis, Writing – review & editing.

Maylin Malter: Methodology, Writing – review & editing. **Konstanze Stübner:** Methodology, Writing – review & editing. **Florian Adolphi:** Conceptualization, Methodology, Writing – review & editing, Supervision, Project administration, Funding acquisition.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

Data will be made available on request.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.nimb.2023.165179>.

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