

## Simultaneous preconcentration of $^9\text{Be}$ and cosmogenic $^{10}\text{Be}$ for determination of the $^{10}\text{Be}/^9\text{Be}$ ratio in (coastal) seawater

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### Abstract

Beryllium isotopes have emerged as a quantitative tracer of continental weathering, but accurate and precise determination of the cosmogenic  $^{10}\text{Be}$  and stable  $^9\text{Be}$  in seawater is challenging, because seawater contains high concentrations of matrix elements but extremely low concentrations of  $^9\text{Be}$  and  $^{10}\text{Be}$ . In this study, we develop a new, time-efficient procedure for the simultaneous preconcentration of  $^9\text{Be}$  and  $^{10}\text{Be}$  from (coastal) seawater based on the iron co-precipitation method. The concentrations of  $^9\text{Be}$ ,  $^{10}\text{Be}$ , and the resulting  $^{10}\text{Be}/^9\text{Be}$  ratio for Changjiang Estuary water derived from the new procedure agree well with those obtained from the conventional procedure requiring separate preconcentration for  $^9\text{Be}$  and  $^{10}\text{Be}$  determinations. By avoiding the separate preconcentration, our newly developed procedure contributes toward more time-efficient handling of samples, less sample cross-contamination, and a more reliable  $^{10}\text{Be}/^9\text{Be}$  ratio. Prior to this, we validated the iron co-precipitation method using artificial seawater and natural water samples from the Amazon Estuary regarding: (1) the “matrix effect” for Be analysis, (2) its extraction efficiency for  $\text{pg g}^{-1}$  levels Be in the presence and absence of organic matter, and (3) the data comparability with another preconcentration method. We calculated that for the determination of  $^9\text{Be}$  and  $^{10}\text{Be}$  in most open ocean seawater with typical  $^{10}\text{Be}$  concentrations of  $> 500$  atoms  $\text{g}^{-1}$ , good precisions ( $< 5\%$ ) can be achieved using less than 3 liters of seawater compared to more than 20 liters routinely used previously. Even for coastal seawater with extremely low  $^{10}\text{Be}$  concentration (e.g., 100 atoms  $\text{g}^{-1}$ ), we estimate a maximum amount of 10 liters to be adequate.

Cosmogenic beryllium-10 ( $^{10}\text{Be}$ ,  $T_{1/2} = 1.39$  Myr) is produced in the atmosphere at a known rate and reaches Earth's surface and oceans by wet and dry deposition (Willenbring and von Blanckenburg 2010), while its stable counterpart  $^9\text{Be}$

is released from rocks by chemical weathering and is transferred to the oceans mainly by rivers (von Blanckenburg and Bouchez 2014). Due to the particle-reactive nature of Be, more than 90% of Be ( $^9\text{Be}$  and  $^{10}\text{Be}$ ) are trapped in the coastal area when transported to the oceans via rivers (von Blanckenburg and Bouchez 2014). In the oceans, riverine input is the dominant source for  $^9\text{Be}$ , while the river-derived  $^{10}\text{Be}$  is negligible compared to its direct deposition from the atmosphere. The average residence time of Be in seawater is found to be ca. 600–1000 yr, and the distinctly different sources of these two isotopes lead to distinct  $^{10}\text{Be}/^9\text{Be}$  ratios between coastal seawater and open ocean, and between ocean basins (Kusakabe et al. 1987; Bourles et al. 1989; Ku et al. 1990; Brown et al. 1992; Measures et al. 1996; von Blanckenburg and Igel 1999; Frank et al. 2009; Kong et al. 2021b). This makes the  $^{10}\text{Be}/^9\text{Be}$  ratio in seawater a sensitive tracer for intra-oceanic processes, such as water mass mixing

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Additional Supporting Information may be found in the online version of this article.

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(Frank et al. 2002; Frank et al. 2009) and ocean circulation (Kusakabe et al. 1987; Ku et al. 1990; von Blanckenburg et al. 1996).

Nevertheless, applications of the  $^{10}\text{Be}/^9\text{Be}$  ratio in seawater are still very limited due to analytical difficulties. These arise from the extremely low concentrations of beryllium in seawater relative to extremely high concentrations of the seawater matrix that mainly comprises Na, Mg, K, and Ca in  $> 10,000 \mu\text{g g}^{-1}$  concentration ranges. Concentrations of  $^9\text{Be}$  ( $^9\text{Be}$ ), square brackets denote concentrations), however are typically only  $0.03\text{--}0.54 \text{ pg g}^{-1}$  ( $3\text{--}60 \text{ pmol kg}^{-1}$ ) in the open ocean (Measures and Edmond 1982, 1983; Kusakabe et al. 1987; Ku et al. 1990; Measures et al. 1996). Lowest  $^9\text{Be}$  concentrations (ca.  $0.03 \text{ pg g}^{-1}$ ) are found in surface waters from the western equatorial Pacific region (Xu 1994). In estuaries,  $^9\text{Be}$  can reach values of  $\sim 9 \text{ pg g}^{-1}$  ( $1 \text{ nmol kg}^{-1}$ ), due to the high riverine contribution (Measures and Edmond 1983; Brown et al. 1992). For the rare cosmogenic isotope  $^{10}\text{Be}$ , a typical concentration range in open ocean water is  $300\text{--}2000 \text{ atoms g}^{-1}$  (Kusakabe et al. 1987; Ku et al. 1990; Measures et al. 1996; Frank et al. 2009). For coastal seawater, published [ $^{10}\text{Be}$ ] data are limited to four sites: the San Francisco Bay (Kusakabe et al. 1991), the East China Sea (Yang et al. 2003), the northern South China Sea (Kong et al. 2021b), and the Pearl River estuary (Kong et al. 2021a) where  $^{10}\text{Be}$  concentration ranges are  $60\text{--}1000 \text{ atoms g}^{-1}$ . Precise measurements of such low Be concentrations thus require methods that enable the preconcentration of Be, that is, the separation of Be from the seawater matrix and its concentration into a small volume (i.e., a few mL), from easily collectible volumes of a few liters.

Over the past few decades, preconcentration procedures have been routinely carried out separately for  $^9\text{Be}$  and  $^{10}\text{Be}$  for water samples (Measures and Edmond 1982; Kusakabe et al. 1987; Frank et al. 2009; Kong et al. 2021b), that is, by splitting the original water sample into  $^9\text{Be}$  and  $^{10}\text{Be}$  aliquots prior to sample preconcentration (hereafter called the “conventional” procedure). A  $^9\text{Be}$  carrier is then added to the  $^{10}\text{Be}$  split before preconcentration, which is required for accelerator mass spectrometry (AMS) measurements of a  $^{10}\text{Be}/^9\text{Be}_{\text{carrier}}$  ratio. From the known amount of  $^9\text{Be}_{\text{carrier}}$ , the unknown amount of  $^{10}\text{Be}$  in the sample can be calculated, because the amount of  $^9\text{Be}$  added by the carrier is much larger than the natural  $^9\text{Be}$  present in the water sample. In this way, the recovery of  $^{10}\text{Be}$  along the preconcentration steps can be accurately monitored. The most routinely used method for  $^{10}\text{Be}$  preconcentration is the iron co-precipitation method, for which a large volume of seawater of approximately 20 liters is typically required (Kusakabe et al. 1987; Frank et al. 2009; Kong et al. 2021a,b). For  $^9\text{Be}$ , a variety of methods have been employed, including hydroxide co-precipitation (Hiraide et al. 1994), liquid–liquid extraction (Measures and Edmond 1986; Bashir and Paull 2001), micelle-mediated extraction (Afkhani et al. 2007; Beiraghi and Babae 2008), and solid-phase extraction (Amin 2001; Yousefi et al. 2010;

Tazoe et al. 2014). Employed  $^9\text{Be}$  sample volumes vary from 0.1 to 1 liter. Although preconcentrating  $^9\text{Be}$  and  $^{10}\text{Be}$  separately yields a more reliable  $^{10}\text{Be}$  concentration, it is time-consuming, and may introduce uncertainty in the natural  $^{10}\text{Be}/^9\text{Be}$  ratio if Be recovery differs in each split, especially when different preconcentration methods are applied for  $^9\text{Be}$  and  $^{10}\text{Be}$ , respectively.

In this study, we developed a new, time-efficient procedure (hereafter called the “simplified” procedure) to preconcentrate  $^9\text{Be}$  and  $^{10}\text{Be}$  simultaneously using the iron co-precipitation method. We tested this new procedure on a set of natural samples from the Changjiang Estuary that were also analyzed following the conventional procedure. We supplement this new development with several validations of the iron co-precipitation method for Be extraction from seawater that have not been conducted previously: We tested (1) the potential “matrix effect” on Be analysis using a sector-field high-resolution inductively coupled plasma-mass spectrometer (HR-ICP-MS), (2) its extraction efficiency of different  $\text{pg g}^{-1}$ -levels Be in the presence and absence of organic matter, both using artificial seawater, and (3) the data comparability with another entirely different preconcentration method using natural Amazon Estuary water samples. Finally, we estimated the minimum water volume required for precise  $^9\text{Be}$  and  $^{10}\text{Be}$  determination based on the current techniques and methods employed, with the aim to provide references for future studies.

## Materials and procedures

### Reagents

All reagents were used as supplied and checked for possible  $^9\text{Be}$  contamination. Concentrated  $\text{HNO}_3$  and  $\text{HCl}$  used in this study were purified by sub-boiling analytical grade acids (Merck) and then diluted to the required molarity using ultra-pure water ( $18.2 \text{ M}\Omega\text{-cm}$ , Milli-Q, Merck Millipore). The ammonia (25% w/w, Merck, Germany) used is analytical grade. The  $\text{FeCl}_3$  solution was prepared by dissolving iron(III)chloride hexahydrate (VMR Chemicals) in 1 M  $\text{HCl}$ . A 0.4 M oxalic acid solution was prepared by dissolving solids (BioUltra, Sigma-Aldrich) in Milli-Q water. Beryllium-9 concentrations in all reagents were checked to be under the detection limit. A  $^9\text{Be}$  carrier solution with a concentration of  $780 \mu\text{g g}^{-1}$ , prepared from a phenakite mineral obtained from a deep mine (von Blanckenburg et al. 2016), was used to prepare standards for external calibration for the determination of [ $^9\text{Be}$ ].

### Preparation of artificial seawater

For artificial seawater preparation, we added roughly 33.33 g synthetic salt (Dupla Marin Premium Reef Salt Natural Balance, product code DM81432\_MA) into 1 liter Milli-Q water. This mixture mimics the natural composition of seawater and was used as the mother solution in the matrix effect test as well as for the recovery and dissolved organic carbon (DOC) tests.

### Sampling of natural seawater

In the Changjiang (Yangtze) River Estuary, five natural coastal seawater samples were taken along a salinity transect from 0 to 32.0 practical salinity units (PSU) during the Key Elements Cycling in the Changjiang-Estuary-Shelf Transect (KECES; August to September 2019) cruise (Supporting Information Fig. S1). All samples were collected approximately 3–4 m upstream from the ship's bow via a pre-cleaned Masterflex I/P<sup>®</sup> Precision Pump tubing (C-Flex<sup>®</sup>) attached to the front end of a carbon fiber pole sampler, and water was pumped by a peristaltic pump. After collection, samples were immediately filtered through an acid-cleaned 0.45- $\mu\text{m}$  filter (Supor<sup>®</sup> PES, Pall). The filtrates were stored in pre-cleaned Low-density polyethylene (LDPE) bottles (Nalgene), acidified to pH < 2 with trace metal grade HCl, and stored at 4°C until analysis.

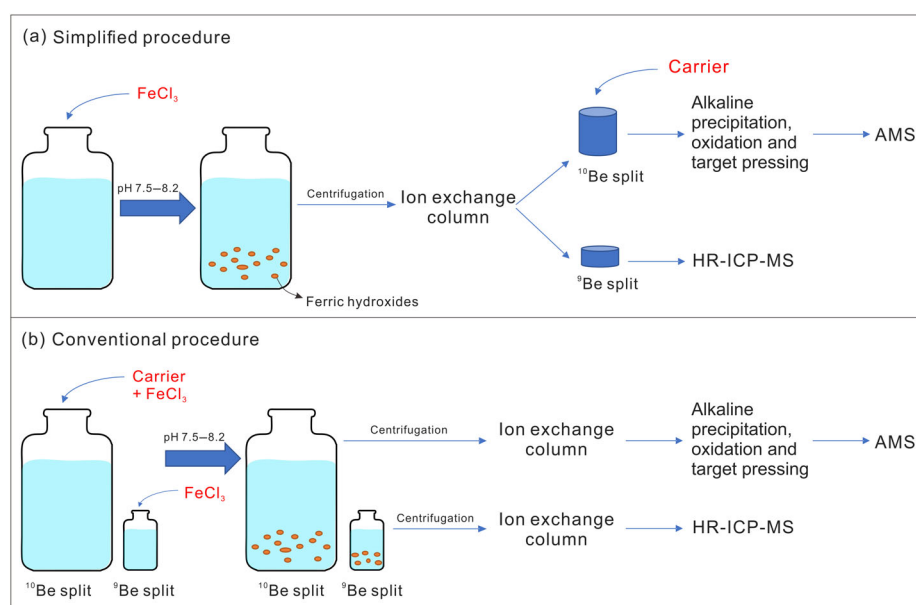
Nine natural coastal seawater samples were collected from the Amazon River Estuary during R/V Meteor Cruise M147 (Amazon-GEOTRACES, May 2018) (Supporting Information Fig. S1). The samples were collected along a salinity transect from 0 to 35.5 PSU using Niskin bottles attached to a rosette equipped with a conductivity–temperature–depth sensor. After collection, samples were filtered within a few hours through 0.45- $\mu\text{m}$  filters (Nucleopore) and acidified to pH  $\sim$  2 with concentrated ultrapure HCl. Samples were stored at room temperature prior to analysis. One sample at station M147\_55-F (salinity of 35.5 PSU) was taken with a towed fish but otherwise treated the same way.

### Preconcentration of $^9\text{Be}$ and $^{10}\text{Be}$

#### Simplified procedure

The iron co-precipitation method was employed for the simultaneous preconcentration of  $^9\text{Be}$  and  $^{10}\text{Be}$  (as illustrated

in Fig. 1a) for water samples. The volume of water required to measure  $^9\text{Be}$  and  $^{10}\text{Be}$  will depend on each isotope's concentration (see discussion later), which varies in the (coastal) oceans. In this study, only around 600 g water were used due to limited available sample volume. In a 1<sup>st</sup> step, about 6 mL  $\text{FeCl}_3$  solution (2 mg  $\text{Fe mL}^{-1}$ ) was added to the sample (i.e., 20 mg  $\text{Fe L}^{-1}$  seawater). In Step 2, after equilibration for > 12 h, the pH was adjusted to 7.5–8.2 (measured by pH indicator paper PEHANON<sup>®</sup> with a measuring range of 7.2–8.8) using diluted ( $\sim$  12.5%) aqueous ammonia. To allow the homogenization and precipitation of Fe-hydroxide, the sample was shaken several times and then left standing overnight. In a 3<sup>rd</sup> step, the precipitate containing Be was separated from the liquid by centrifugation at 4000 rpm for 15 min and rinsed three times with pH 8-adjusted water. Note that for large volume samples (i.e., > 2 liters), we suggest to let the formed precipitate settle by gravity for 2–3 d. The upper supernatant can be gently decanted and the remaining lower supernatant is centrifuged to separate the precipitates. In a 4<sup>th</sup> step, the precipitate was oxidized overnight in 4 mL of aqua regia at 160°C. After evaporation and re-dissolving in 4 mL 6 M HCl, Step 5 of the procedure employs the separation of Fe from Be using a 20-mL column filled with 5 mL Bio-Rad AG<sup>®</sup> 1-X8 (100–200 mesh) anion exchange resin following established anion column chemistry routines (detailed steps are provided in Supporting Information). The Be was collected in 10 mL 6 M HCl, evaporated to dryness and re-dissolved in 6 mL 3 M  $\text{HNO}_3$ . Step 6 employs the splitting of this solution, where a 1 mL aliquot of the solution (1/6 of the solution) was gravimetrically separated and evaporated, then re-dissolved in 1 mL 3%  $\text{HNO}_3$ , and spiked with 1 ng  $\text{g}^{-1}$



**Fig. 1.** Simplified scheme for the “simplified” (a) and the “conventional” (b) procedures for preconcentrating  $^9\text{Be}$  and  $^{10}\text{Be}$  from seawater using the iron co-precipitation method. The “ion exchange column” is a Biorad AG 1-X8 anion exchange column used for separating Fe from Be.

Rhodium (Rh) as internal standard for  $^9\text{Be}$  analysis. The concentration factor (i.e., the ratio of the sample's initial volume to the volume of analyte for measurement) was approximately 100 times. In Step 7, the remaining 5 mL (5/6 of the solution) were spiked with 0.15 mg  $^9\text{Be}$  carrier and prepared for  $^{10}\text{Be}$  determination on the AMS. This entails evaporation and re-dissolving in 10 mL 1 M  $\text{HNO}_3$ , followed by alkaline precipitation, that is, another pH adjustment to 9–10 by adding around 2.5 mL diluted aqueous ammonia (roughly 0.22–0.25 mL ammonia to each mL 1 M  $\text{HNO}_3$ ). After shaking, the centrifuge tube was placed in a warming bath at 65°C for 1 h to allow the precipitation of  $\text{Be}(\text{OH})_2$ . The Be hydroxide precipitate was separated by centrifugation at 4000 rpm for 5 min. After discarding the supernatant, the precipitate was re-dissolved in 5 mL 1 M  $\text{HNO}_3$  and the alkaline precipitation was repeated once. The final collected Be precipitate was rinsed two times by pH 9-adjusted water and re-dissolved in 0.4 mL  $\text{AgNO}_3$  solution containing 3.64 mg Ag. The solution was transferred into a quartz crucible and dried down on the hotplate at  $\sim 110^\circ\text{C}$ , followed by oxidation to BeO and AMS target preparation, for  $^{10}\text{Be}$  determination.

### Conventional procedure

In the conventional procedure (Fig. 1b), the seawater samples were first gravimetrically separated into splits of ca. 180 and 600 g each for  $^9\text{Be}$  and  $^{10}\text{Be}$  preconcentration. Note that the total sample volume employed in this procedure is slightly larger than in the simplified procedure, with the aim to derive more precise values as a benchmark for assessing the reliability of the new, simplified procedure. After adding the  $^9\text{Be}$  carrier to the  $^{10}\text{Be}$  split, both splits were processed individually as described above, that is, addition of  $\text{FeCl}_3$ , pH-dependent Fe-hydroxide precipitation, centrifugation of the precipitate, and anion column chemistry, followed by  $^9\text{Be}$  and  $^{10}\text{Be}$  determination using HR-ICP-MS and AMS, respectively.

### Instrumentation

The  $^9\text{Be}$  was determined on HR-ICP-MS (Element2, Thermo Fisher Scientific) operated in low-resolution mode. Typical instrument operating conditions are shown in Supporting Information Table S1. Under these conditions, the doubly charged ion rate was less than 3% and the oxide rate was less than 5%. Rh was used as an internal standard and Be was quantified by an external calibration with standards prepared gravimetrically from our in-house carrier solution.

Beryllium-10 concentrations were obtained from AMS measurements of  $^{10}\text{Be}/^9\text{Be}_{\text{carrier}}$  ratios at University of Cologne, relative to the standards KN01-6-2 and KN01-5-3 with a  $^{10}\text{Be}/^9\text{Be}$  ratio of  $5.35 \times 10^{-13}$  and  $6.32 \times 10^{-12}$ , respectively (Dewald et al. 2013).

The Na, Mg, K, and Ca concentrations remaining in solutions after preconcentration were determined by an optical emission inductively-coupled plasma spectrometer (ICP-OES,

Varian 720-ES with axial optics) using the 589.592, 280.270, 766.491, and 422.673 nm wavelengths, respectively, and quantified by an external calibration prepared from single-element standards.

### Experimental setup for iron co-precipitation method validation

#### Matrix effect test

To test the potential matrix effects on HR-ICP-MS analysis from the cations remaining in the precipitate after iron co-precipitation, we first checked the major cation composition of the precipitate obtained after the iron co-precipitation. Four artificial seawater samples ( $\sim 100$  g each) were split from the same mother solution and treated according to the preconcentration procedure Steps 1–6 described above. An aliquot of around 50  $\mu\text{L}$  was gravimetrically pipetted out of the HR-ICP-MS split (Step 6) and diluted to 4 mL using 0.3 M  $\text{HNO}_3$  doped with 1000  $\mu\text{g g}^{-1}$  Cs for the measurement of the remaining major cations using ICP-OES and an external calibration. In a 2<sup>nd</sup> approach, we employed the standard addition method (see Supporting Information) to check if remaining cations affect the accuracy of the HR-ICP-MS measurements. Two artificial seawater samples ( $\sim 100$  g each) were separated from the same artificial seawater mother solution. After Step 6 of the iron co-precipitation procedure,  $[\text{Be}]$  was determined from one sample directly (using an external calibration), whereas the other sample was further separated equally into four aliquots, spiked with  $\sim 0$ , 50, 100, and 150  $\text{pg g}^{-1}$  of Be, respectively, and quantified by standard addition.

#### Recovery in the presence and absence of DOC

Since no certified water standard is available for  $^{10}\text{Be}$  and AMS analysis is costly and time-consuming, we carried out a recovery test in the presence and absence of DOC using  $^9\text{Be}$ -spiked artificial seawater, with the aim to evaluate the effect of DOC on Be recovery during the iron co-precipitation method. We assume that our test results are equally valid for  $^{10}\text{Be}$ , given the identical geochemical behavior of  $^9\text{Be}$  and  $^{10}\text{Be}$  and their negligible isotope fractionation during co-precipitation. Although additional procedures are required for  $^{10}\text{Be}$  determination after the iron co-precipitation, any potential loss of the  $^{10}\text{Be}$  thereafter can be controlled by the addition of a  $^9\text{Be}$  carrier.

A set of artificial seawater samples (each  $\sim 100$  g) were split from the mother solution of artificial seawater and spiked with ascending Be concentrations, that is, 0, 5, 10, and 20  $\text{pg g}^{-1}$ . The unspiked sample was used to monitor Be background levels in the mother solution (see Supporting Information). Procedural blanks using  $\sim 100$  g Milli-Q water were also processed. In addition, a set of duplicate Be-spiked samples were supplied with 0.2 g of 0.4 M oxalic acid, resulting in a DOC concentration of 160  $\mu\text{M}$  to mimic the maximum value

for open ocean and most coastal seawater (Hansell et al. 2009; Barrón and Duarte 2015).

The Be recovery (%) was calculated by subtracting the Be concentration of the unspiked sample from the measured concentrations of spiked samples and compared them with the added Be concentration (data are shown in Supporting Information Table S2). Subtraction of the unspiked sample resulted from finding non-negligible amounts of  $^9\text{Be}$  already present in the salt used to prepare the mother solution (see Supporting Information).

### Data comparability test

To further benchmark the iron co-precipitation method against previously employed methods, we applied the iron co-precipitation method to natural coastal seawater samples collected along a salinity gradient in the Amazon Estuary and compared our data to previously published data determined by electron capture detection gas chromatography after the liquid-liquid extraction.

## Assessment and discussion

### Matrix effect

An essential purpose of the preconcentration process is to remove the high seawater matrix prior to analysis. The HR-ICP-MS measurement for  $^9\text{Be}$  has been considered highly sensitive to matrix effects (Kawaguchi et al. 1987; Tan and Horlick 1987). First, Be is particularly sensitive to space-charge effects as low-mass elements are more affected than heavier mass elements, causing a loss of sensitivity (Archuleta and Duran 2009). Second, the matrix may affect the sample transport and ionization efficiency into the plasma and thus suppress the signal of the analyte (Archuleta and Duran 2009).

The composition of the remaining matrix (mainly Na, Mg, K, and Ca) in the analytes (1 mL 3%  $\text{HNO}_3$  spiked with  $1 \text{ ng g}^{-1}$  Rh, Step 6 in the iron co-precipitation procedure) is shown in Table 1. Mean concentration values found for Na, Mg, and Ca were around 6, 31, and  $38 \mu\text{g g}^{-1}$ , respectively, while the K concentration is below detection limit. Considering a concentration factor of about 100, this indicates that

more than 99% of the initial seawater matrix was removed during the iron co-precipitation procedure.

By means of standard addition, we examined whether these  $\mu\text{g g}^{-1}$  levels of matrix remaining in solution after preconcentration will affect the analysis of  $^9\text{Be}$  by HR-ICP-MS. The  $^9\text{Be}$  concentration in an artificial seawater sample obtained using standard addition is  $2.72 \pm 0.18 \text{ pg g}^{-1}$  (see details in the Supporting Information), which is in good agreement with the directly measured value of  $2.93 \pm 0.08 \text{ pg g}^{-1}$  using an external calibration. This indicates that the remaining matrix in solution after iron co-precipitation does not affect the  $^9\text{Be}$  determination via HR-ICP-MS.

### Be recovery and effects of DOC

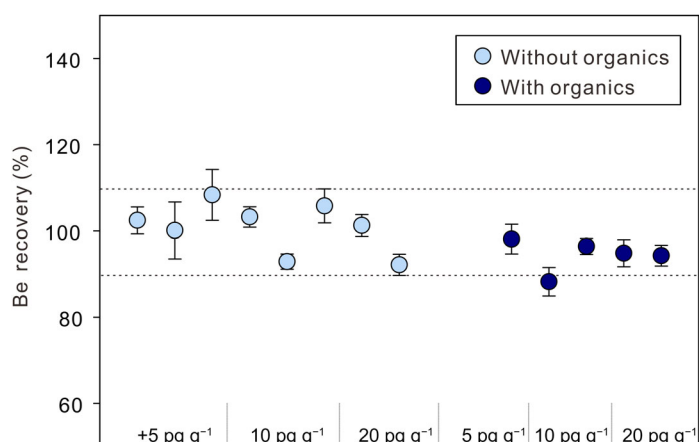
Across a pH range of 6–9, the majority of Be exists as hydrolyzed species when humic acid is absent. However, in the presence of humic acid, Be is instead found to be speciated as Be-humate (Takahashi et al. 1999; Willenbring and von Blanckenburg 2010). Based on mixing experiments, Suhrhoff et al. (2019) proposed that DOC may stabilize Be in the dissolved phase, thus the Be-humate complexes are more resistant to colloidal flocculation during estuarine mixing. Therefore, it is likely that the alteration of aqueous Be species may influence the behavior of Be during the co-precipitation process, resulting in reduced recovery efficiency. Reduced Be recovery ( $\sim 30\%$ ) has been reported after adding  $1600 \mu\text{M}$  (ca.  $20 \text{ mg L}^{-1}$ ) DOC to river water (Wittmann et al. 2015). However, a typical DOC concentration range is 34 to  $\sim 80 \mu\text{M}$  ( $0.4$  to  $\sim 1 \text{ mg L}^{-1}$ ) for open ocean seawater (Hansell et al. 2009) and 40 to  $> 700 \mu\text{M}$  ( $0.5$  to  $> 8 \text{ mg L}^{-1}$ ) in coastal water (Barrón and Duarte 2015). In our experiment we thus added  $160 \mu\text{M}$  (ca.  $2 \text{ mg L}^{-1}$ ) DOC, which comprises a maximum value for open ocean and most coastal seawater.

Resulting mean recovery for the Be concentration range between 5 and  $20 \text{ pg g}^{-1}$  in the absence of DOC is  $100.8\% \pm 5.7\%$  (1 SD,  $N = 8$ ) (Fig. 2). This recovery does not depend on the spiked Be concentration and is comparable to previously reported values (Suhrhoff et al. 2019). Note, however, that Suhrhoff et al. (2019) used a single spiked Be concentration

**Table 1.** Concentrations of Na, Mg, K, and Ca in artificial seawater samples before and after the iron co-precipitation.

		Na ( $\mu\text{g g}^{-1}$ )	Mg ( $\mu\text{g g}^{-1}$ )	K ( $\mu\text{g g}^{-1}$ )	Ca ( $\mu\text{g g}^{-1}$ )
Initial concentration		11,000	1300	390	420
Sample ID	Initial seawater weight (g)				
AFSW_1	100.4	n.d.	36	n.d.	33
AFSW_2	100.1	2	35	n.d.	43
AFSW_3	100.1	1	27	n.d.	38
AFSW_4	100.3	21	27	0.3	39

The initial concentrations of Na, Mg, K, and Ca are theoretical concentrations derived from the ingredients of the synthetic salt mixture. The concentrations of Na, Mg, K, and Ca in artificial seawater (AFSW) samples are measured concentrations in analytes after preconcentration, the concentration factors are about 100 times. For ICP-OES measurements, a 5% uncertainty is given that represents the long-term repeatability. n.d. = measured value is lower than the detection limit.



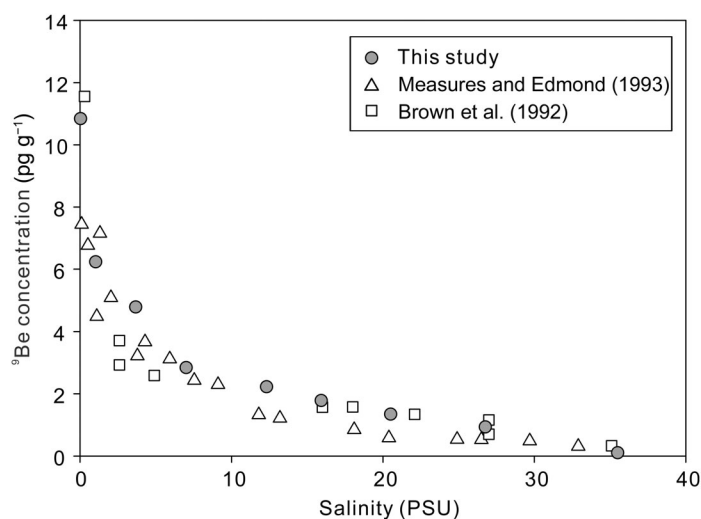
**Fig. 2.** Long-term recovery of  $^9\text{Be}$  from artificial seawater spiked with different  $^9\text{Be}$  concentrations in the absence and presence of organic matter (simulating a seawater DOC concentration of  $160\ \mu\text{M}$  by addition of oxalic acid); Dashed lines represent recovery within  $100\% \pm 10\%$ .

(i.e.,  $9\ \text{pg g}^{-1}$ ) and did not evaluate a Be concentration range. In the presence of DOC, the mean Be recovery is with  $95.2\% \pm 3.9\%$  (1 SD,  $N = 6$ ) (Fig. 2) slightly lower, but nearly identical to that obtained in the absence of organics. We regard this somewhat lower recovery to be unproblematic, because (1) this narrow range of  $\pm 5\%$  is well within the range of commonly encountered uncertainties of such low-level analytics, and (2) a lower recovery will not affect the ratio of  $^{10}\text{Be}$  to  $^9\text{Be}$ , as both isotopes will be equally affected.

Overall, this assessment demonstrates that the Be recovery will not be affected by the presence of up to  $160\ \mu\text{M}$  of organic matter. This implies that for open ocean seawater and the majority of coastal seawater where DOC concentrations are below  $160\ \mu\text{M}$ , the iron co-precipitation method can be applied directly without a previous decomposition of organic matter. However, for water with much higher DOC concentrations, a lower Be recovery may be expected, and obtained single [ $^{10}\text{Be}$ ] or [ $^9\text{Be}$ ] may be treated with caution.

#### Data comparability between the iron co-precipitation method and the liquid–liquid extraction method

Various preconcentration methods have been employed for  $^9\text{Be}$  determination in seawater in previous studies, but the comparability of data derived from these methods still remains unclear. Dissolved  $^9\text{Be}$  concentrations in the Amazon Estuary seawater (Supporting Information Table S3; Fig. 3) obtained using the iron co-precipitation method, show good agreement with previously published data (Fig. 3), both displaying an exponential decrease with salinity. The previous data obtained by Measures and Edmond (1983) and Brown et al. (1992) were both determined by electron capture detection gas chromatography after liquid–liquid extraction. This good agreement confirms the data comparability between the iron co-precipitation method (commonly employed to obtain  $^{10}\text{Be}$  concentrations)



**Fig. 3.** Dissolved  $^9\text{Be}$  concentrations (in  $\text{pg g}^{-1}$ ) in the Amazon Estuary along a salinity transect from 0 to 35.5 PSU. Error bars for this study are smaller than the symbol size, and not available for published studies. Samples from Brown et al. (1992) were collected during the AMASEDS Expedition in August 1989.

and the liquid–liquid extraction method that is widely used to obtain  $^9\text{Be}$  concentrations. This demonstrates that the iron co-precipitation method is suitable to generate comparable and oceanographically consistent Be data.

#### Application of the simplified procedure to natural coastal seawater

After validation of the ion co-precipitation method, we next employ it to determine the  $^{10}\text{Be}/^9\text{Be}$  ratio in five coastal seawaters collected from the Changjiang Estuary, following the new simplified procedure (Fig. 1a). To provide a benchmark, we also measured the same samples following the conventional procedure (Fig. 1b). Compared to the conventional procedure, the simplified procedure has the following advantages: (1) *Improved time-efficiency*. The co-precipitation and the subsequent column chemistry routines only need to be performed once, as compared to twice in the conventional procedure. (2) *Reduced cross-contamination*. In the conventional procedure, the  $^9\text{Be}$  carrier that has a much higher  $^9\text{Be}$  concentration than natural seawater is added to the  $^{10}\text{Be}$  split before the preconcentration (Fig. 1b) and hence may contaminate the  $^9\text{Be}$  split by any accidental or mixed-use of the laboratory consumables (e.g., beakers, columns) that are employed for  $^9\text{Be}$  and  $^{10}\text{Be}$  preconcentration, respectively. This risk can be reduced by employing the simplified procedure. (3) *Improved reliability of the  $^{10}\text{Be}/^9\text{Be}$  ratio*. Preconcentrating  $^9\text{Be}$  and  $^{10}\text{Be}$  simultaneously can avoid any potential unproportionate loss of  $^9\text{Be}$  and  $^{10}\text{Be}$  during co-precipitation and the chromatographic steps, thus resulting in more reliable  $^{10}\text{Be}/^9\text{Be}$  ratio. The only disadvantage of the simplified procedure is that the absolute value of [ $^{10}\text{Be}$ ] can be potentially biased, given that

**Table 2.** Dissolved (diss)  $^9\text{Be}$  and  $^{10}\text{Be}$  concentrations and resulting  $^{10}\text{Be}/^9\text{Be}$  ratios for five coastal seawater samples from the Changjiang Estuary following the conventional and the simplified preconcentration procedures.

Sample ID	Salinity (PSU)	Conventional procedure				Simplified procedure				
		Initial seawater mass for $^9\text{Be}$ (g)	Initial seawater mass for $^{10}\text{Be}$ (g)	$[^9\text{Be}]_{\text{diss}}^*$ (pg g $^{-1}$ )	$[^{10}\text{Be}]_{\text{diss}}^\dagger$ (atoms g $^{-1}$ )	$(^{10}\text{Be}/^9\text{Be})_{\text{diss}}^\ddagger$ ( $\times 10^{-9}$ )	Initial seawater mass for $^9\text{Be}$ and $^{10}\text{Be}$ (g)	$[^9\text{Be}]_{\text{diss}}^*$ (pg g $^{-1}$ )	$[^{10}\text{Be}]_{\text{diss}}^\dagger$ (atoms g $^{-1}$ )	$(^{10}\text{Be}/^9\text{Be})_{\text{diss}}^\ddagger$ ( $\times 10^{-9}$ )
C1	0.1	182	610	1.30 $\pm$ 0.06 (4.2%)	195 $\pm$ 32 (16.4%)	2.24 $\pm$ 0.38	664	1.06 $\pm$ 0.04 (3.4%)	188 $\pm$ 36 (19.1%)	2.65 $\pm$ 0.51
C6-2	4.1	181	611	0.88 $\pm$ 0.03 (3.7%)	177 $\pm$ 35 (19.8%)	3.00 $\pm$ 0.61	600	0.83 $\pm$ 0.03 (3.6%)	227 $\pm$ 37 (16.3%)	4.10 $\pm$ 0.68
C6-3	9.3	179	620	0.96 $\pm$ 0.03 (3.4%)	235 $\pm$ 35 (14.9%)	3.66 $\pm$ 0.56	600	0.89 $\pm$ 0.04 (4.5%)	276 $\pm$ 38 (13.8%)	4.66 $\pm$ 0.67
C9	16.8	185	627	0.88 $\pm$ 0.09 (10.0%)	205 $\pm$ 35 (17.1%)	3.50 $\pm$ 0.61	601	0.85 $\pm$ 0.02 (2.4%)	196 $\pm$ 33 (16.8%)	3.45 $\pm$ 0.59
C18	32.0	194	599	0.27 $\pm$ 0.02 (5.2%)	149 $\pm$ 33 (22.1%)	8.28 $\pm$ 3.20	600	0.31 $\pm$ 0.04 (12.9%)	132 $\pm$ 32 (24.2%)	6.47 $\pm$ 1.79

\*Uncertainty is the analytical uncertainty (1 SD) from HR-ICP-MS analysis in absolute and relative (%) numbers.

$^\dagger$ Uncertainty contains analytical uncertainty (1 SD) from AMS measurement, and sample ratios were corrected using a mean long-term blank ( $^{10}\text{Be}/^9\text{Be}_{\text{blank}}$  ratio of 1.62 ( $\pm 1.07$ , 1 SD)  $\times 10^{-15}$  ( $N = 4$ ).

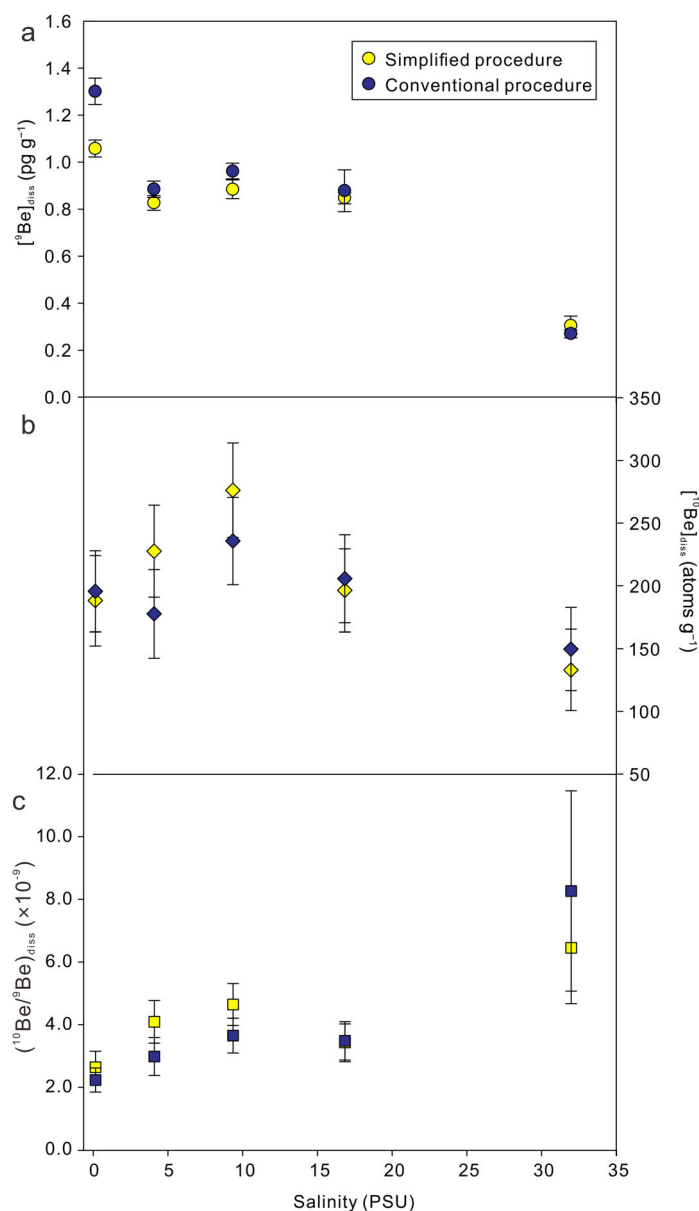
$^\ddagger$ Uncertainty was propagated from the given  $[^9\text{Be}]$  and  $[^{10}\text{Be}]$  uncertainties.

the potential loss during the co-precipitation and the chromatographic steps cannot be controlled without having added the  $^9\text{Be}$  carrier before. However, the results for  $[^9\text{Be}]$ ,  $[^{10}\text{Be}]$  and the resulting  $^{10}\text{Be}/^9\text{Be}$  ratio of five coastal Changjiang seawater samples obtained from these two procedures (Fig. 1) agree well with each other (Table 2; Fig. 4). Except for one sample at close-to-zero salinity where the difference in  $[^9\text{Be}]$  amounts to 18% (Fig. 4a), nearly all variations are within the uncertainties (albeit in some cases large). The relatively large uncertainties in the  $^{10}\text{Be}$  concentrations result from the extremely low concentrations in the samples and minimized sample volumes of only 500–600 g (see the next section). The good agreement between data obtained by the two procedures indicates nevertheless high accuracy results from both procedures. It can be inferred that our simplified procedure is equally feasible for obtaining accurate concentrations of  $^9\text{Be}$  and  $^{10}\text{Be}$  and  $^{10}\text{Be}/^9\text{Be}$  ratios, in comparison with the time-consuming conventional procedure. We therefore recommend this simplified procedure for future studies on Be isotopes in seawater, especially when only the  $^{10}\text{Be}/^9\text{Be}$  ratio is of interest.

#### Water sample volume required for $^9\text{Be}$ and $^{10}\text{Be}$ determination

Due to the extremely low concentrations of  $^9\text{Be}$  and  $^{10}\text{Be}$  in seawater as observed in the Changjiang Estuary, a large volume of sample is required for more accurate determination. Note that > 20 liters was routinely employed in former studies. However, sampling and processing of large volumes of seawater is time-consuming and labor-intensive. Hence, it is worthwhile to estimate a minimum volume for accurate determination before sampling or planning an experiment.

In this study, the detection limit (LOD) for  $^9\text{Be}$  is 29.7 pg g $^{-1}$ , calculated using the average procedural blank signal plus three times the standard deviation ( $N = 14$ ). Combining this LOD with the lowest  $^9\text{Be}$  concentration of 0.027 pg g $^{-1}$  so far reported for open ocean seawater (Xu 1994), a sample volume of 1.1 liters would allow to detect even lowest  $^9\text{Be}$  concentrations in nearly all types of seawater samples. However, in order to achieve good precision and accuracy (i.e., relative standard deviation < 5%) of  $^9\text{Be}$  determination, using a limit of quantification (LOQ, calculated using the average instrumental blank signal plus 10 times the standard deviation,  $N = 14$ ) of 50.2 pg g $^{-1}$  in this study would necessitate a sample volume of 1.8 liters. When measured on estuarine water with a typical  $^9\text{Be}$  concentration of > 0.13 pg g $^{-1}$  (Measures and Edmond 1983; Kusakabe et al. 1991; Brown et al. 1992; Kong et al. 2021a), a sample volume of < 0.4 liters would be sufficient for accurate  $^9\text{Be}$  determination. The higher uncertainties (> 5%) observed for sample C18 from the Changjiang Estuary (Table 2) are examples for failing to reach the LOQ due to the inadequate sample volume employed (0.19 and 0.1 liters used for the conventional and the simplified procedures, respectively). It is worth noting that the LOD and LOQ for  $^9\text{Be}$  determination may vary greatly between different



**Fig. 4.** Comparison of dissolved  $^9\text{Be}$  (A),  $^{10}\text{Be}$  (B), and  $(^{10}\text{Be}/^9\text{Be})$  (C) for five coastal seawater samples from the Changjiang Estuary along a salinity transect where  $^9\text{Be}$  and  $^{10}\text{Be}$  were preconcentrated following the conventional and the simplified procedures, respectively. Data are shown in Table 2.

laboratories even if the same technique is employed, depending on the laboratory environment and instrument status. Therefore, measuring a series of blanks to define the LOD and LOQ should precede planning a sampling campaign.

For  $^{10}\text{Be}$ , typical lower limits of the  $(^{10}\text{Be}/^9\text{Be})$  ratio are  $10^{-15}$  to  $10^{-16}$  at most AMS facilities (Müller et al. 2008; Klein et al. 2011). However, the detection limit that matters is set by the laboratory procedural blanks which account for  $^{10}\text{Be}$

contained in the carrier and possibly introduced during sample processing. To our best of knowledge this type of detection limit data has to date not been reported for the analysis of  $^{10}\text{Be}$  in seawater samples. In this study we derived an average  $(^{10}\text{Be}/^9\text{Be})_{\text{blk}}$  value from four procedural blanks corresponding to four sample batches processed between May 2020 to October 2020. From this average  $(^{10}\text{Be}/^9\text{Be})_{\text{blk}}$  value of  $1.62 (\pm 1.07, 1 \text{ SD}) \times 10^{-15}$ , we calculated a “ $^{10}\text{Be}$ -LOD” of  $4.83 \times 10^{-15}$  and a “ $^{10}\text{Be}$ -LOQ” of  $1.23 \times 10^{-14}$ . The minimum seawater sample volume ( $M_{\text{seawater}}$ , in g) used for preconcentration required for AMS determination can be roughly calculated based on the following equation:

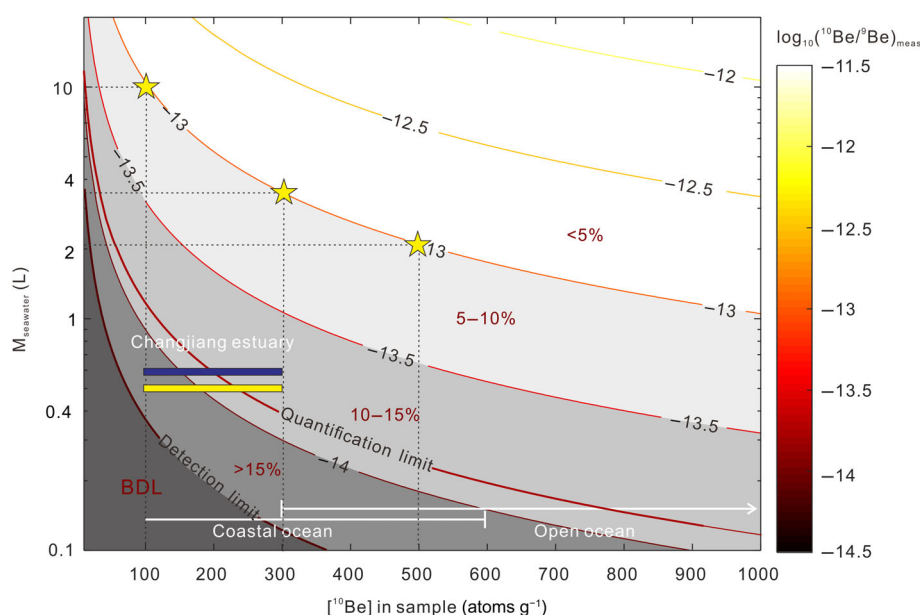
$$M_{\text{seawater}} = \frac{M_{\text{carrier}} \times \frac{N_A}{M_{^9\text{Be}}} \times \left( \left( \frac{^{10}\text{Be}}{^9\text{Be}} \right)_{\text{meas}} - \left( \frac{^{10}\text{Be}}{^9\text{Be}} \right)_{\text{blk}} \right)}{[^{10}\text{Be}]} \quad (1)$$

where  $[^{10}\text{Be}]$  is the  $^{10}\text{Be}$  concentration ( $\text{atoms g}^{-1}$ ) in the sample,  $M_{\text{carrier}}$  is the weight of added  $^9\text{Be}$  carrier (g),  $N_A$  is Avogadro’s number ( $1 \text{ mol}^{-1}$ ),  $M_{^9\text{Be}}$  is the molar weight of  $^9\text{Be}$  ( $\text{mol g}^{-1}$ ),  $(^{10}\text{Be}/^9\text{Be})_{\text{meas}}$  is the measured AMS (carrier) ratio of the sample and  $(^{10}\text{Be}/^9\text{Be})_{\text{blk}}$  is the mean AMS-derived blank ratio. A correction for natural  $^9\text{Be}$  concentration is not necessary since the concentration of  $^9\text{Be}$  in seawater is negligible compared to that of the  $^9\text{Be}$  carrier.

Employing Eq. (1) and using our long-term mean  $(^{10}\text{Be}/^9\text{Be})_{\text{blk}}$  value of  $1.62 \times 10^{-15}$  and a  $M_{\text{carrier}}$  of 0.16 mg (in accordance with the laboratory protocol), for seawater with a  $[^{10}\text{Be}]$  of  $100 \text{ atoms g}^{-1}$  (which denotes nearly the minimum concentration present in seawater), a minimum of 0.4 liters of sample will be needed to achieve  $(^{10}\text{Be}/^9\text{Be})_{\text{meas}}$  to be higher than the  $^{10}\text{Be}$ -LOD, but around 1 liter to meet the  $^{10}\text{Be}$ -LOQ (Fig. 5). However, even if the  $^{10}\text{Be}$ -LOQ is reached, the uncertainty calculated for the final  $[^{10}\text{Be}]$  is still significant (i.e.,  $> 10\%$ ), because it is not only derived from the analytical uncertainty of AMS-derived  $(^{10}\text{Be}/^9\text{Be})_{\text{meas}}$  (typically  $> 10\%$  when  $^{10}\text{Be}$  counts are less than 100), but also propagated from the non-negligible uncertainty of the mean blank ratio. Our  $[^{10}\text{Be}]$  data obtained from the Changjiang Estuary exemplify such “minimum volume” conditions, resulting in high uncertainties (Table 2, and yellow and blue bars in Fig. 5). Means to reduce the uncertainty would be to either lower the procedural blank value to  $10^{-16}$ , or to increase the sample volume. For example, to reduce the uncertainty of the Changjiang samples to  $< 5\%$ , a sample volume of around 4 to 10 liters would be required (Fig. 5). For open ocean seawater with a typical  $^{10}\text{Be}$  concentration of  $> 500 \text{ atoms g}^{-1}$ , only around 2 liters of sample would be sufficient to achieve a final uncertainty of  $< 5\%$ .

These calculations demonstrate that there is no need to collect more than 20 liters of seawater for  $^9\text{Be}$  and  $^{10}\text{Be}$  determinations as done by previous studies, but that around 3 liters (2 liters for  $^{10}\text{Be}$  and 1 liter for  $^9\text{Be}$  when following the conventional preconcentration procedure) of open ocean seawater





**Fig. 5.** Visualization of Eq. (1) calculated using the long-term mean blank ratio  $(^{10}\text{Be}/^9\text{Be})_{\text{blk}} = 1.62 (\pm 1.1, 1 \text{ SD}) \times 10^{-15}$  atoms atoms $^{-1}$  and  $M_{\text{carrier}} = 0.16$  mg (see the text). Toward the lower left side, uncertainties (%) of calculated  $[^{10}\text{Be}]$  propagated from the blank ratio- and empirical analytical AMS-related uncertainties increase, as indicated by the red numbers. The LOQ in this case is  $1.2 \times 10^{-14}$  atoms atoms $^{-1}$ , and the LOD is  $4.8 \times 10^{-15}$  atoms atoms $^{-1}$ , with “BDL” (below detection limit) indicating ranges not detectable. The blue and yellow bars indicate the data range we obtained from the Changjiang Estuary when around 0.6 liters (blue) and 0.5 liters (yellow) of seawater were processed following the conventional and simplified procedures, respectively. The yellow stars indicate the water volumes required to yield accurate  $^{10}\text{Be}$  concentrations for the Changjiang Estuary seawater and open ocean seawater with a  $[^{10}\text{Be}]$  of 500 atoms  $\text{g}^{-1}$ . The white segments below represent the typical range of  $[^{10}\text{Be}]$  in coastal and open ocean seawater.

and a maximum of 10 liters (9.5 liters for  $^{10}\text{Be}$  and 0.5 liters for  $^9\text{Be}$ ) for coastal seawater would be sufficient.

When following the simplified procedure, that is, pre-concentrating  $^9\text{Be}$  and  $^{10}\text{Be}$  from a single volume of water, the splitting strategy (Step 6) after the iron co-precipitation should be based on the relative estimated sample volumes required for accurate  $^9\text{Be}$  and  $^{10}\text{Be}$  determinations. For example, if 3 liters (2 liters for  $^{10}\text{Be}$  and 1 liter for  $^9\text{Be}$ ) of open ocean seawater would be needed, splitting the solution after anion exchange column should be in proportion of 2 : 1 (2/3 for  $^{10}\text{Be}$  and 1/3 for  $^9\text{Be}$  determination, respectively).

### Comments and recommendations

The iron co-precipitation method is a robust pre-concentration procedure capable of quantitatively recovering ultra low-level Be from open ocean and most coastal seawater (dissolved organic carbon levels lower than  $160 \mu\text{M}$ ) in the range of a few  $\text{pg g}^{-1}$ . We show that (1) the matrix effect for HR-ICP-MS determination from remaining cations after the iron co-precipitation is negligible; and (2) data derived from the iron co-precipitation method is comparable with those derived from the liquid-liquid extraction method. Our new procedure based on the iron co-precipitation method to pre-concentrate  $^9\text{Be}$  and  $^{10}\text{Be}$  simultaneously from seawater is found to be equally feasible for obtaining accurate concentrations of  $^9\text{Be}$  and  $^{10}\text{Be}$  and  $^{10}\text{Be}/^9\text{Be}$  ratios in comparison with

the conventional procedure where  $^9\text{Be}$  and  $^{10}\text{Be}$  require separate pre-concentration. We recommend this simplified procedure for future analysis on  $^{10}\text{Be}/^9\text{Be}$  ratios in the ocean, as it saves time and avoids potential sample cross-contamination and unproportionate loss of  $^9\text{Be}$  and  $^{10}\text{Be}$  during separate pre-concentration. We also provide means to estimate the required minimum sample volume for precise  $^9\text{Be}$  and  $^{10}\text{Be}$  determinations before sampling or planning an experiment. If an approximate concentration range of  $^9\text{Be}$  and  $^{10}\text{Be}$  in the sample is unknown, we recommend to use about 3 and 10 liters of water volume for open ocean seawater and coastal seawater, respectively.

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### Conflict of Interest

None declared.

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