



A new method for precise determination of iron, zinc and cadmium stable isotope ratios in seawater by double-spike mass spectrometry



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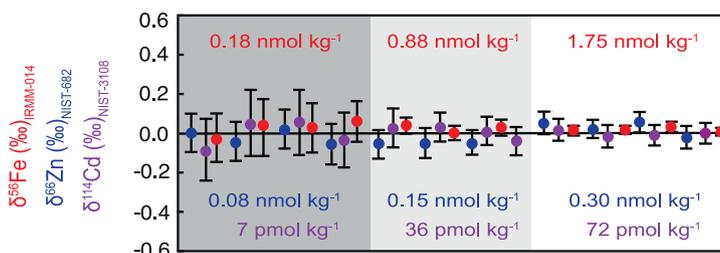
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HIGHLIGHTS

- The first simultaneous method for isotopic analysis of Fe, Zn and Cd in seawater.
- Designed for 1 L samples, a 1–20 fold improvement over previous methods.
- Low blanks and high precision allow measurement of low concentration samples.
- Small volume and fast processing are ideal for high-resolution large-scale studies.
- Will facilitate investigation of marine trace-metal isotope cycling.

GRAPHICAL ABSTRACT

'Metal-free' seawater doped with varying concentrations of 'zero' isotope standards, processed through our simultaneous method, and then analyzed by double spike MC-ICPMS for Fe, Zn and Cd isotope ratios. All values were determined within 2 σ error (error bars shown) of zero.



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ABSTRACT

The study of Fe, Zn and Cd stable isotopes ($\delta^{56}\text{Fe}$, $\delta^{66}\text{Zn}$ and $\delta^{114}\text{Cd}$) in seawater is a new field, which promises to elucidate the marine cycling of these bioactive trace metals. However, the analytical challenges posed by the low concentration of these metals in seawater has meant that previous studies have typically required large sample volumes, highly limiting data collection in the oceans. Here, we present the first simultaneous method for the determination of these three isotope systems in seawater, using Nobias PA-1 chelating resin to extract metals from seawater, purification by anion exchange chromatography, and analysis by double spike MC-ICPMS. This method is designed for use on only a single litre of seawater and has blanks of 0.3, 0.06 and <0.03 ng for Fe, Zn and Cd respectively, representing a 1–20 fold reduction in sample size and a 4–130 decrease in blank compared to previously reported methods. The procedure yields data with high precision for all three elements (typically 0.02–0.2‰; 1 σ internal precision), allowing us to distinguish natural variability in the oceans, which spans 1–3‰ for all three isotope systems. Simultaneous extraction and purification of three metals makes this method ideal for high-resolution, large-scale endeavours such as the GEOTRACES program.

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1. Introduction

First row transition metals are known to occupy key roles in ocean biogeochemical cycles [1]. It is now well established that

iron (Fe) is a necessary micronutrient for plankton and that low dissolved Fe concentrations (0.02–2 nmol kg⁻¹) limit primary productivity over much of the surface ocean, significantly influencing the global carbon cycle and climate [2]. Other transition metals, such as zinc (Zn) and cadmium (Cd) also act as both nutrients and/or toxins for phytoplankton [3,4]. Despite the analytical challenges associated with the low dissolved concentration of these metals in the ocean (p-nmol kg⁻¹), measurement of concentration

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has become a routine chemical oceanographic tool [5,6], with large-scale undertakings such as the GEOTRACES project now generating multi-element high-resolution datasets. However, these operationally defined measurements of concentration do not always provide complete information about sources, sinks and cycling of these metals within the ocean, leaving a gap in our knowledge of marine biogeochemical cycles. Many natural low-temperature processes fractionate stable isotopes by mass, and so the study of isotopic ratios of these metals offers the potential to further constrain cycling, sources and sinks of these metals in the ocean.

In the last decade, advances in technique and the introduction of multi-collector inductively coupled plasma mass spectroscopy (MC-ICPMS) have made it possible to determine trace metal isotope ratios ($\delta^{56}\text{Fe}$, $\delta^{66}\text{Zn}$ and $\delta^{114}\text{Cd}$) at concentrations found in the natural environment. Many studies have aimed to characterize the signatures of sources of Fe to the oceans, in the form of crustal composition, loess, aerosol dust, hydrothermal vents, porewaters, and ferromanganese crusts [7–15]. These studies suggest that it is possible to use isotope ratios to both fingerprint sources, and to constrain the relative magnitude of their fluxes to the ocean; for example, the $\delta^{56}\text{Fe}$ of bulk crustal ($\sim 0\%$) [8] and atmospheric dust ($\sim 0.2\%$) [16] are very different to both that of anoxic pore fluids (-3.4 to -0.6%) [9,12,15,17,18] and hydrothermal vent fluids (-0.67 to -0.09%) [7,11,14]. Several authors have reported biological fractionation of Zn and Cd isotopes in cultured phytoplankton and higher plants [19–23], suggesting that $\delta^{66}\text{Zn}$ and $\delta^{114}\text{Cd}$ will trace biological processes including nutrient cycling and nutrient utilization, in both present and past oceans [24].

More recently, the development of clean and effective chemical separation and the ability to resolve interferences (e.g. ArO^+ on ^{56}Fe) with a high-resolution mode have allowed measurement of $\delta^{56}\text{Fe}$, $\delta^{66}\text{Zn}$ and $\epsilon^{114}\text{Cd}$ with the precision necessary ($<0.2\%$) to directly measure these ratios in seawater [13,25–30]. The first studies of $\delta^{56}\text{Fe}$, $\delta^{66}\text{Zn}$ and $\epsilon^{114}\text{Cd}$ in seawater [26,31–38] demonstrate the promise of these measurements as new oceanographic tracers and their use to fingerprint sources and trace processes. For example, recent studies have directly fingerprinted the addition of Fe from dust ($\delta^{56}\text{Fe} = 0.3\%$) [37], reduced Fe(II) ($\delta^{56}\text{Fe} = -1.82\%$) [36] or oxic sediments ($\delta^{56}\text{Fe} = 0.36\%$) [39] to seawater, observed strong biological fractionation of Cd isotopes by biological activity [33,34,40], or noted as-yet unexplained excursions in $\delta^{66}\text{Zn}$ in the sub-surface [26,41], which may illuminate Zn cycling in the surface oceans.

The first studies of trace metal isotopes in seawater also highlight the significant challenges associated with analysis. The low concentrations [5,6] of Fe (0.02 – 2 nmol kg^{-1} ; ~ 1 – 110 ng kg^{-1}), Zn (0.05 – 8 nmol kg^{-1} ; ~ 3 – 500 ng kg^{-1}) and especially Cd (<1 – 500 pmol kg^{-1} ; ~ 0.1 – 50 ng kg^{-1}) in seawater, relative to the potential for contamination during sampling, limits signal size and therefore places direct limits on analytical precision [30]. The sea-salt matrix contains high concentrations of elements that generate interferences (e.g. Ni^+ , Cr^+ , CaO^+ , ArSi^+ , MoO^+) and suppress signal voltage during MC-ICPMS analysis, prohibiting direct injection of samples into the plasma. Studies have therefore used methods to separate and purify the metal of interest from the sea-salt matrix before analysis by multi-collector ICPMS. Previous approaches include co-precipitation with Al [26] or Mg [13] and resin ion-exchange chromatography [28,30,42]. These studies have typically utilized large volumes of seawater (1 – 20 L) [28,29,31,26], in order to overcome high blanks or detection limits or to reduce analytical uncertainty. John and Adkins [30] recently published a method to determine $\delta^{56}\text{Fe}$ in a single litre of seawater using NTA resin with bulk extraction, and a similar approach is employed here.

This work presents a new method using Nobias PA-1 chelating resin to simultaneously extract Fe, Zn and Cd from 1 L seawater,

followed by purification on a single anion-exchange column, and separate-element analysis by Thermo Neptune MC-ICPMS.

2. Materials and method development

2.1. Reagents and equipment

All sample preparation work was carried out in flow benches with Ultra Low Penetration Air (ULPA) filtration at the University of South Carolina. All reagents (HCl , HNO_3 , HBr , H_2O_2 , NH_4OH) were Aristar Ultra™ (UP) obtained from VWR International, and all water used was $>18.2 \text{ M}\Omega$ from a Barnstead purification system. All PFA Teflon filtration apparatus and vials were obtained from Savillex, and new equipment was cleaned by sequential soaking at least overnight in 1% Citrad detergent, warm 50% (v/v) quartz distilled (QD) HNO_3 , warm 50% (v/v) QD HCl , warm 0.1% QD HNO_3 and warm 3 N HNO_3 , with extensive rinsing with water between steps. PFA equipment was stored in 0.1% (v/v) UP HNO_3 between uses. All low density polyethylene (LDPE) was cleaned by immersion in 1% Citrad detergent, followed by one week soaking in 10% (v/v) reagent grade HCl , with extensive rinsing between steps. In order to minimize Zn contamination, all clean equipment was handled with polyethylene gloves.

2.2. Metal extraction from seawater

Metals were extracted from seawater using a bulk-extraction technique [30] with Nobias PA-1 chelating resin, obtained from Hitachi High Technologies, Japan. This resin has been used in several previous studies for extraction of both trace metals [5,43] and REE [44], and combines high affinity for trace metals compared to major salt cations (Mg, Na, Ca) with low blank contamination. The resin consists of methacrylate polymer beads, with both EDTriA and IDA acid functional groups [43], both of which bind strongly to transition metal ions [5]. Previous studies [5,43], using in-line flow systems, estimated $>98\%$ recovery of Fe, Zn and Cd at pH ~ 6 – 6.5 , with just $<1\%$ recovery of major salt cations. Other studies have used NTA [45,46] or IDA [6] resins to extract metals from seawater, but we find these to have higher blanks and lower affinities for Zn than Nobias PA-1. Testing of drip-through and in-line extraction with both Nobias PA-1 and Toyopearl IDA resin, compared to bulk extraction with Nobias PA-1, demonstrated reduced efficiencies for Zn and Cd in the former compared to the latter.

The full procedure is shown in Table 1; briefly, 2.5 mL ($\sim 0.78 \text{ g}$) of clean Nobias resin was added to 1 L of pH 2 seawater, which was then shaken vigorously for 2 h, the pH adjusted to 6.15 ± 0.2 , the seawater shaken again for 2 h, and then metals eluted from the resin with $\sim 25 \text{ mL}$ of 3 M HNO_3 . New Nobias resin was cleaned as described in Table 1. Cleaned resin was used multiple times, with storage in 3 M HNO_3 between uses. Sample pH was adjusted by addition of 2 mL (per L of seawater) of an ammonium acetate solution, made from ultrapure water, UP 17 M acetic acid and UP 11 M $\text{NH}_4\text{OH}_{(\text{aq})}$ in a 1:1.1:1.75 ratio (5.0 M), and then adjusted to 6.15 ± 0.2 (final buffer strength 0.01 M) by addition of 11 M UP $\text{NH}_4\text{OH}_{(\text{aq})}$. Buffer design was based on Sohrin et al. [43], with the final buffer strength reduced to reduce blank contribution. The two-step procedure was chosen both to maximize extraction efficiency of Zn and Cd, which do not bind to the resin at low pH (Table 2), and to minimize precipitation of Fe during pH adjustment to pH 6. A shaking time of two hours rapid shaking was chosen based on a previous study, which showed that after 2 h $>95\%$ of metals were bound to an NTA resin [30]. A pH of 6.15 was chosen based on experimentation and comparison to other studies [5,43]. It was determined that 25 mL of 3 M HNO_3 was sufficient to elute $>99\%$ of all the metals from the resin (Fig. 1), but that weaker HNO_3 was not as effect

Table 1

A procedural outline for extraction and purification of Fe, Zn and Cd from seawater for MC-ICPMS isotopic analysis.

Extraction of Fe, Cd and Zn from seawater with Nobias PA-1 resin	
1.	Clean new Nobias resin by leaching in 3 changes of 3 M HNO ₃ over a week.
2.	Rinse pre-cleaned resin with 3 × 50 mL ultrapure water.
3.	Add ⁵⁷ Fe– ⁵⁸ Fe, ⁶⁴ Zn– ⁶⁷ Zn and ¹¹⁰ Cd– ¹¹¹ Cd double spikes to 1 L seawater sample (pH 1.7–2; 10 μM H ₂ O ₂) 24 h before extraction.
4.	Add 2.5 mL pre-cleaned resin and vigorously shake sample for at least 2 h (Fe).
5.	Adjust pH to 6.15 ± 0.2 with CH ₃ COONH ₃ and NH ₄ OH.
6.	Vigorously shake samples for at least 2 h (Zn, Cd).
7.	Pour sample through filter to separate resin.
8.	Rinse resin with 125 mL ultrapure water.
9.	Elute metals with 5 × 5 mL 3 M HNO ₃
10.	Evaporate samples at 200 °C. Reconstitute and reflux in 200 μL of aqua regia to dissolve organics for 2 h.
11.	Evaporate samples at 200 °C. Reconstitute in 200 μL of 10 M HCl + 0.001% H ₂ O ₂ for purification by anion exchange chromatography.
Purification by anion-exchange chromatography	
1.	Add 20 μL of pre-cleaned AG-MP1 resin to PTFE micro-columns.
2.	Clean resin with 4 × 250 μL 10 M HCl + 0.001% H ₂ O ₂ .
3.	Rinse resin with 5 × 60 μL ultrapure water.
4.	Condition column with 2 × 100 μL 10 M HCl + 0.001% H ₂ O ₂ .
5.	Add sample.
6.	Elute salts and Cu in 5 × 20 μL 10 M HCl + 0.001% and 12 × 20 μL 5 M HCl + 0.001% H ₂ O ₂ (see Fig. 2).
7.	Elute Fe in 8 × 20 μL 1 M HCl.
8.	Elute Zn in 12 × 20 μL 2 M HNO ₃ + 0.1 M HBr
9.	Elute Cd in 10 × 20 μL 2 M HNO ₃
10.	Evaporate samples and reconstitute in 1–5 mL of 0.1 M HNO ₃ for MC-ICPMS analysis.

Table 2

Extraction efficiency and blanks (±1SD); for details, see text.

Element	Extraction efficiency (%)		Extraction blank (ng)	Purification blank (ng)	Total blank (ng)
	pH 2	pH 2 and 6			
Fe	66	78	0.12 ± 0.06	0.16 ± 0.09	0.28
Cd	2	101	0.004 ± 0.002	<0.001	0.004
Zn	7	102	0.06 ± 0.09	<0.005	0.064
Ni	nd	92 ± 7	0.09 ± 0.12	nd	nd
Pb	nd	72 ± 4	<0.01	nd	nd
Cu	nd	80 ± 1	0.08 ± 0.05	nd	nd
Co	nd	69 ± 4	nd	nd	nd
Mn	nd	103 ± 3	nd	nd	nd

ive; Zn and Cd were observed to stay bound to the resin with 1 M HCl.

Procedural blanks were estimated for Fe and Zn (and Cu, Ni and Pb) by processing 2 × 1 of 0.4 μm filtered GEOTRACES North Atlantic seawater (pH adjusted and kept at 6.15 ± 0.15) through the bulk extraction technique five times to remove any metal ('metal-free seawater') and then processing five additional times using the

same procedure applied to samples. To avoid MoO⁺ interferences on Cd, Cd blanks were estimated by leaching 2.5 mL of clean Nobias resin five times with 3 M HNO₃. All blanks were analyzed by Thermo Element II sector field ICPMS using a 100 μL min⁻¹ borosilicate glass nebulizer, glass cyclonic spraychamber without desolvation, standard Ni sampler and Ni 'H' skimmer cone.

2.3. Sample purification

Following extraction, samples were purified by anion-exchange chromatography. This procedure was previously optimized for low Fe concentrations by reducing resin volume [30]. Here, two previously published anion-exchange purification methods are combined in order to simultaneously purify Fe, Zn and Cd at low concentrations (<1–400 ng) [47,48]. The full procedure is described in Table 1; briefly, metals were loaded onto 20 μL of cleaned AG-MP1 resin in PTFE Teflon micro-columns and then salts + Ni + Cu, Fe, Zn and Cd were eluted sequentially in different reagents (the elution scheme is shown in Fig. 2). Samples were then dried down and re-dissolved in 15 mL LDPE tubes for analysis by MC-ICPMS. Procedural blanks for purification were estimated for Cd, Fe and Zn by loading five columns with 200 μL of clean 10 M HCl + 0.001% (v/v) H₂O₂ and processing them as samples. The key strength of this approach is effective purification of Ni and salts from Fe and Zn, Sn and Mo from Cd (<10% of Sn and <0.1% Mo elute with Cd) and quantitative recovery of all three metals of interest (Cd 104%, Fe 101%, Zn 99%).

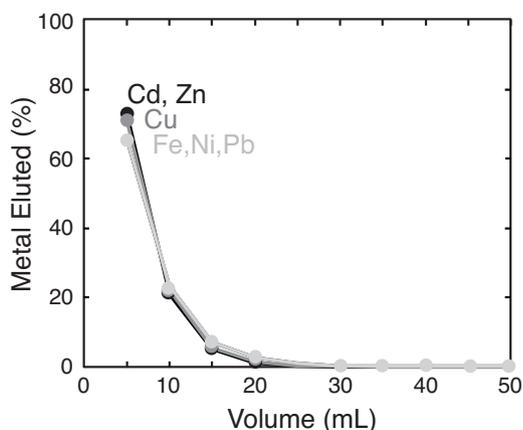


Fig. 1. Elution of transition metals from Nobias PA-1 chelating resin, in 5 mL aliquots of 3 M HNO₃.

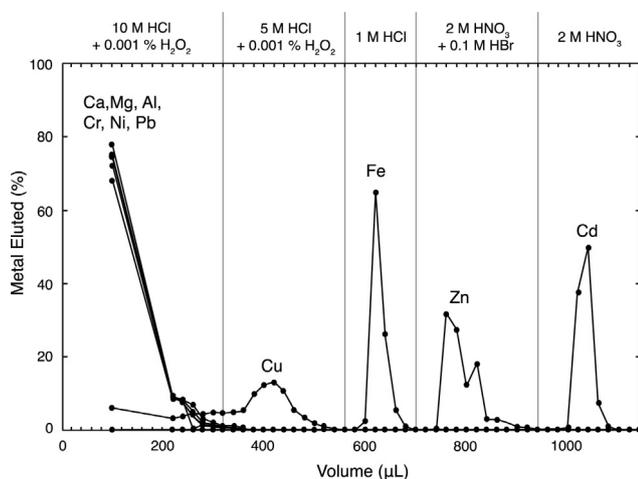


Fig. 2. Elution scheme for purification of sample by AGMP-1 resin micro-column. The first point represents concentrations in 200 μL eluent collected during sample loading, and subsequent points represent sequential elution in 20 μL aliquots. Na, K, Ba and rare earth elements elute with Ca, Mg and Al. For more details, see Table 1.

2.4. Isotopic analyses

2.4.1. Instrumental setup

All isotopic ratios were determined using a Thermo Neptune MC-ICPMS with an ESI Apex-Q introduction system, without a desolvation membrane, at the Center for Elemental Mass Spectrometry at the University of South Carolina. A jet interface (Thermo Scientific), with a Pt Jet and an Al 'x-type' skimmer cone, was used both to maximize sensitivity and reduce Ni isobaric interferences on Fe and Zn, which may result from Ni cones. The low concentration of these metals in seawater means that every attempt must be made to maximize sensitivity and reduce background. Standards and samples were introduced using a $\sim 100\text{--}150\ \mu\text{L}\ \text{min}^{-1}$ borosilicate glass nebulizer. A range of washout times and acids were tested, and it was found that rinsing for 2 min in 5% (v/v) QD- HNO_3 and 1 min in 0.1 M QD- HNO_3 between samples was most effective at reducing memory effects. Signal intensity was recorded over 50 cycles of 4.2 s. Typically, the first 12–15 cycles were discarded to account for uptake and stabilization time, leaving 35–38 cycles (147–160 s) per analysis. Each isotope ratio was calculated as a mean average of the 38 cycles, and cycles which were $>3\times$ the SD were discarded. Analyses were corrected for instrumental background by subtracting the average blank signal, measured over 38 cycles in a 0.1 M HNO_3 solution, with each group of 5 samples bracketed by two blank measurements.

2.4.2. Resolution of polyatomic interferences and correction for isobaric interferences

Cd was measured in 'low resolution' mode (LR) and both Fe and Zn in 'high resolution' mode (HR), using a high resolution slit (25 μm), in order to resolve polyatomic interferences (e.g. ArN^+ on ^{54}Fe , ArO^+ on ^{56}Fe and ArOH^+ on ^{57}Fe , and ArSi^+ on ^{67}Zn ; see Table S-1, Supplementary Information). Typical representative sensitivities for ^{56}Fe (HR), ^{64}Zn (HR) and ^{110}Cd (LR) were 0.17, 0.14 and 1.12 V ppb^{-1} respectively. Each isotope of Fe (or Zn) was resolved from any respective polyatomic interferences by measurement of the signal voltage on the left flat shoulder/plateau of the combined metal-argide peak, following the technique of Weyer and Schwieters [49]. This technique is based on the principle that all polyatomic interferences in this mass range are heavier than Fe or Zn, and so, with sufficient resolving power, the left side of the peak is free from polyatomic interferences [49].

Based on theoretical prediction [49] and observation (this study [30]), a resolution of >6000 ($m/\Delta m$; 5–95% of the side of the peak) on the Neptune multicollector is sufficient to resolve polyatomic argide interferences adequately from Fe, except at very low concentrations ($<10\ \text{ng}\ \text{g}^{-1}$; see below). Resolution >6000 can only be achieved with the 'high' $\sim 25\ \mu\text{m}$ resolution slit ($>8000\ m/\Delta m$; 5–95% of the side of the peak), with the low ($\sim 250\ \mu\text{m}$) and medium ($\sim 50\ \mu\text{m}$) resolution slits typically only providing ~ 1000 or $\leq 5000\ m/\Delta m$ respectively. Even with measurement on the left shoulder in high resolution ($>8000\ m/\Delta m$; 5–95% of the side of the peak), a small proportion of the ArO^+ and ArN^+ interferences were observed to be still present at 54 and 56 masses, at levels that had the potential to influence low-concentration ($<10\ \text{ng}\ \text{g}^{-1}$) samples. To address this, an Ar/CH_4 mixture (9:1) was introduced directly into the Apex through the nitrogen inlet port at a flow rate of $20\ \text{mL}\ \text{min}^{-1}$. Addition of Ar/CH_4 reduced $^{40}\text{Ar}^{16}\text{O}^+$ by 80%, $^{40}\text{Ar}^{14}\text{N}^+$ by 64% and Fe by 28%, reducing the mass width of the interference peaks, and allowing more complete resolution of the polyatomic interferences from Fe.

To correct for isobaric interferences, signal intensity was measured for each isotope system at the masses shown in the relevant cup-configuration in Table S-1 (Supplementary Information). Cr and Ni isobaric interferences on ^{54}Fe and ^{58}Fe were corrected for by measuring the abundances of ^{53}Cr and ^{60}Ni , Ni on Zn by measuring ^{60}Ni , and Pd and Sn on Cd by measuring ^{105}Pd and ^{117}Sn (Table S-1, Supplementary Information). Day-to-day variability in instrumental mass bias has an insignificant effect on these corrections, so the mass bias was measured once and applied thereafter.

The high concentration of Mo in seawater ($9\text{--}11\ \mu\text{g}\ \text{L}^{-1}$) [50] and the mass range of MoO^+ (108–116 amu) combine to create potentially significant interferences for all Cd isotopes except ^{106}Cd . Some studies [6] have made corrections for MoO^+ on both Cd isotope ratios and Cd concentrations, but this is challenging given the mass dispersion and number of Faraday cups on the Neptune. No correction was made for MoO^+ isotopes on these samples, as it was determined that such corrections are insignificant. The method described herein extracts $\sim 5\%$ of Mo from seawater, of which $<0.1\%$ elutes with the Cd fraction during purification, and of Mo atoms introduced to the plasma only $\sim 0.1\%$ form MoO^+ species which could interfere with Cd. Monte Carlo simulation [51] suggests that this quantity of MoO^+ has an insignificant effect on $\delta^{114}\text{Cd}$.

2.4.3. Mass bias correction and double spikes

Isotopic fractionation within the MC-ICPMS (instrumental mass bias) may be corrected for in several ways – either by measuring ratios in an element of similar mass and properties (e.g. Ni on Fe [30]) together with sample-standard bracketing or through the use of a 'double spike' [52]. The latter involves the addition of a mixture of two highly purified isotopes of the element of interest, present in a very non-natural ratio. Use of a double spike not only allows for correction of instrumental mass bias but has two key advantages over sample-standard bracketing: (1) addition of double spike prior to processing allows for correction of any procedural fractionation if yields are not quantitative; (2) isotope dilution can be used to determine initial concentration very accurately when the spike addition is well constrained. Four isotopes in the sample-spike mixtures are then used to calculate three independent ratios (e.g. $^{54}\text{Fe}/^{57}\text{Fe}$, $^{56}\text{Fe}/^{57}\text{Fe}$, $^{58}\text{Fe}/^{57}\text{Fe}$), which allows for the calculation of three unknowns, namely the sample-spike ratio, procedural/instrumental isotopic fractionation, and the isotopic fractionation of a sample relative to the standard, assuming all fractionation follows the mass dependence law. Solutions of pure natural isotope standard ($\text{Fe}_{\text{IRMM-014}}$, $\text{Zn}_{\text{NIST-682}}$ and $\text{Cd}_{\text{NIST-3108}}$) and pure double spike were analyzed twice at the beginning of each analytical session, and the measured isotope ratios were entered as

the three spike and sample ratios required for the data reduction scheme.

Double spikes were prepared from purified mono-isotopic solutions of ^{57}Fe (96.6%), ^{58}Fe (99.9%), ^{64}Zn (99.7%), ^{67}Zn (89.6%), ^{110}Cd (95.6%), and ^{111}Cd (97.2%), obtained from Isoflex USA. Each double spike solution was designed with an isotopic composition optimized to minimize error during data reduction, based on errors calculated by Monte Carlo simulation [53]. The Fe double spike used comprised 0.003% ^{54}Fe , 0.7% ^{56}Fe , 47.7% ^{57}Fe , and 51.6% ^{58}Fe , the Zn double spike used comprised 80% ^{64}Zn , 0.9% ^{66}Zn , 18.4% ^{67}Zn and 1% ^{68}Zn and the Cd double spike used comprised 33.4% ^{110}Cd , 64.8% ^{111}Cd , 1.4% ^{112}Cd and 0.4% ^{114}Cd . Double spike concentrations were determined by isotope dilution with purchased concentration standards (accurate to ± 0.1 –1%), measured by ICPMS. Concentrated double spike solutions were purified using 2.5 mL of AGMP-1 resin, with a scheme scaled-up from the procedure outlined in Table 1. Sample-spike ratios (Fe 1:2; Zn and Cd 1:4) were optimized with relatively high spike concentrations, both to increase analytical precision and reduce the potential impact of isobaric interferences [51].

2.4.4. Standard solutions and isotope ratio calculation

Stable isotope ratios were calculated as the average over 35–38 cycles using a data reduction scheme following the iterative approach of Siebert et al. [52]. The low concentration of metal in seawater samples meant that, typically, each sample was analyzed twice, and an average value calculated. Mixtures of the appropriate isotope standard and double spike, designed to match the concentration and sample-spike ratio of the samples, bracketed each group of 5 samples. Ratios are expressed in per mil (‰) relative to the average of these standards, using delta notation ($\delta^{56}\text{Fe}$, $\delta^{66}\text{Zn}$, $\delta^{114}\text{Cd}$) as described in Eq. (1):

$$\delta^{56}\text{Fe}, \delta^{66}\text{Zn}, \delta^{114}\text{Cd} (\text{‰}) = \left[\left(\frac{R_{\text{sample}}}{R_{\text{standard}}} \right) - 1 \right] \times 1000 \quad (1)$$

where R denotes $^{56}\text{Fe}/^{54}\text{Fe}$, $^{66}\text{Zn}/^{64}\text{Zn}$ or $^{114}\text{Cd}/^{110}\text{Cd}$, and the standards are IRMM-014 Fe, Lyon JMC Zn or NIST-3108 Cd. Previous studies on seawater [31,54,55] have expressed Cd isotope ratios in ε units, but δ units are used here so that data can be more easily compared between isotope systems, particularly because the relative mass difference between 56 and 54, 66 and 64, and 114 and 110 is similar, and there is a similar magnitude of variability within each isotope system in seawater.

During each analytical session, standards were run at a range of concentrations and sample-spike ratios. In practice, it was found that no corrections for sample-spike ratio were necessary. However, standards analyzed at different concentrations may have different measured isotope ratios, such that it is desirable to match standard and sample concentration, especially when samples are $< 5 \text{ ng g}^{-1}$ for Cd and $< 10 \text{ ng g}^{-1}$ for Fe and Zn. For the in-house isotope standards, used in each analytical session, the well-established IRMM-014 Fe, NIST-682 Zn and the relatively new but recently intercalibrated [56] NIST-3108 Cd were used. Zn isotope ratios are traditionally expressed relative to Lyon JMC Zinc, which is now difficult to obtain. Lyon JMC Zn $\delta^{66}\text{Zn}$ was determined to be $+2.46\%$ (SD 0.02‰, $n = 10$) compared to NIST-682, indistinguishable from previously published values ($\delta^{66}\text{Zn} = +2.45\%$) [57], and therefore a correction of $+2.46\%$ has been applied to all data such that they can be expressed relative to Lyon JMC Zn.

2.4.5. Determination of metal concentration in seawater samples

The concentration of natural Fe, Zn or Cd in a sample was determined simultaneously with the isotope ratios, based on the known volume of each seawater sample and the quantity of added spike, using isotope dilution equations.

3. Results and discussion

3.1. Accuracy and precision of isotopic analyses

By comparison of theoretically predicted internal error, using Monte Carlo simulation, and measured internal error on $\delta^{56}\text{Fe}$ during analysis of IRMM-014 – Fe double spike mixtures by Neptune MC-ICPMS, it has been shown that internal error with the double spike technique can be described by a combination of Johnson noise and counting statistics [51]. That study also showed predicted and measured internal error was comparable for natural seawater samples, based on isotope analyses of 48 samples of North Atlantic seawater, processed using the method described here. Fig. 3 shows typical internal precision for seawater analyses, with comparable values for predicted internal error from Monte Carlo simulation [51] and measured internal standard error of 93 (Fe), 110 (Zn) or 100 (Cd) North Atlantic Seawater samples (a subset of which were published by John [51]). Measured 1σ internal precision for all three isotope systems ($\delta^{56}\text{Fe}$ 0.01–0.2‰; $\delta^{66}\text{Zn}$ 0.01–0.2‰; $\delta^{114}\text{Cd}$ 0.02–0.7‰; Fig. 3) across the range of concentrations expected in open-ocean seawater is significantly smaller than the expected range of isotopic variability for each element in seawater (2–3‰) [26,31,36,37,39].

In order to test the accuracy and external error of the procedure, ‘metal-free’ seawater (prepared as in Section 2.2) was doped with several concentrations of isotope standards and double spike, designed to represent the expected range of concentrations in natural seawater, and then this doped seawater was processed through the entire method. $\delta^{56}\text{Fe}$, $\delta^{66}\text{Zn}$ and $\delta^{114}\text{Cd}$ analyses were within calculated 2σ internal error of the isotope standard (Fig. 4) for all concentrations, indicating that there is no systematic source of inaccuracy. To further test analytical accuracy, the separations between the in-house isotope standards (IRMM-014 Fe, NIST-682 Zn and NIST-3108 Cd) and several external isotope standards for each isotope system were determined, and the averages and 2σ standard deviations ($n = 10$ for each value) are reported here. For Fe, NIST-3126 Fe was determined to be $0.32 \pm 0.02\%$, relative to IRMM-014, which is similar to that measured by Rouxel and Auro [32]. For Zn, Lyon JMC Zn was $+2.46 \pm 0.02\%$ and Accutrace Zn was -6.69 ± 0.02 , relative to NIST-682 Zn, which are equivalent to previously published values ($+2.45\%$ and -6.69 ± 0.04) [57]. For Cd, a $\delta^{114}\text{Cd}$ value of $-1.367 \pm 0.06\%$ was determined for BAM 1012 and a value of $+4.486 \pm 0.06\%$ was determined for Münster Cd, relative to NIST-3108, which are in good agreement with those reported by Abouchami et al. ($-1.332 \pm 0.04\%$ and $4.499 \pm 0.05\%$) [56].

Based on the match between theoretical and measured 1σ internal error (Fig. 3; [51]), and the excellent external accuracy of isotope ratios in both doped seawater and isotope standards, we find that external sources of error are negligible, and that the main source of uncertainty on these values is internal analytical error caused by Johnson noise and counting statistics. Consequently, uncertainty for this method is expressed based on the standard internal error of each 160s Neptune analysis, and the internal error of standards. Each isotopic ratio was calculated relative to the average of two bracketing isotope standards (1σ errors of σ_{std1} and σ_{std2}). 1σ error for each analysis ($1\sigma_{\text{corr}}$) was therefore calculated as in Eq. (2), using error propagation, where σ_{sam} or σ_{std} represent the standard internal error of a sample or bracketing isotope standard over a single 160s analysis.

$$1\sigma_{\text{corr}} = \sqrt{\sigma_{\text{sam}}^2 + \frac{(\sigma_{\text{std1}})^2 + (\sigma_{\text{std2}})^2}{4}} \quad (2)$$

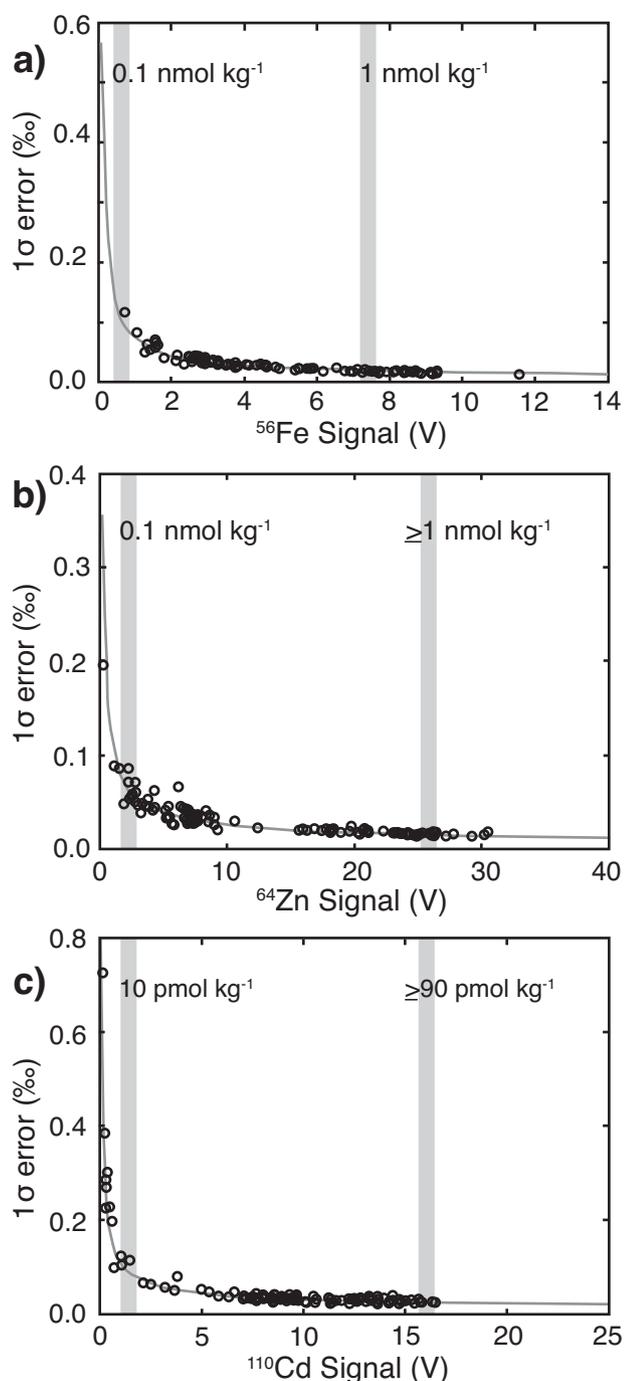


Fig. 3. Theoretical (grey line) versus measured (black points) 1σ internal precision for (a) $\delta^{56}\text{Fe}$, (b) $\delta^{66}\text{Zn}$ and (c) $\delta^{114}\text{Cd}$ compared to MC-ICPMS signal. Theoretical values were calculated using Monte Carlo simulation, assuming sample:spike of 1:2 (Fe) or 1:4 (Zn, Cd). Measured values are 1σ internal standard error from MC-ICPMS analyses of North Atlantic seawater. Signal is shown for one isotope for each element (sample + spike). Precision is shown over the typical range of concentrations of these metals in seawater; vertical grey bars denote the seawater concentration that corresponds to signal intensity (assuming 80% extraction for Fe and 100% for Zn and Cd, and a representative sensitivity; see Section 2.4.2). For Zn and Cd, higher concentrations were diluted to $\sim 90\text{ pmol kg}^{-1}$ or $\sim 1\text{ nmol kg}^{-1}$ for analysis.

Each sample was typically measured twice for isotopic ratio, and a mean value presented.

The final 2σ internal error ($2\sigma_{\text{final}}$) of the mean value was calculated using Eq. (3), where $1\sigma_{\text{corr1}}$ and $1\sigma_{\text{corr2}}$ are the propagated

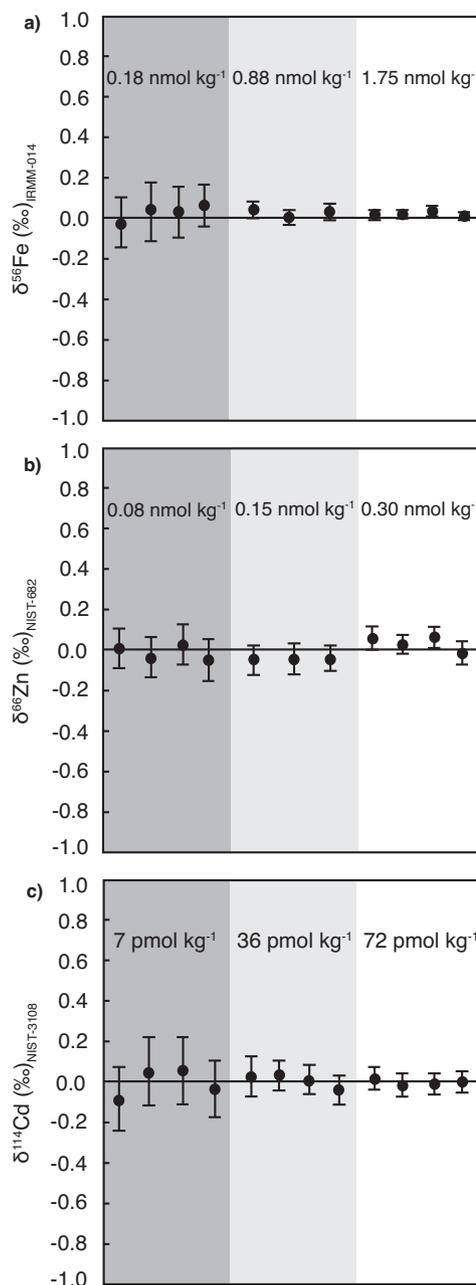


Fig. 4. Measured (a) $\delta^{56}\text{Fe}$, (b) $\delta^{66}\text{Zn}$ and (c) $\delta^{114}\text{Cd}$ in 'metal-free' seawater doped with varying concentrations of in-house isotope standard (IRMM-014 Fe, NIST-682 Zn and NIST-3108 Cd), then extracted, purified, and analyzed as a sample. Each point is the average of two MC-ICPMS analyses, with 2σ error bars shown (calculated as described in the text).

1σ error for each individual analysis with two bracketing standards (from Eq. (2)).

$$2\sigma_{\text{final}} = 2 \times \sqrt{\frac{(\sigma_{\text{corr1}})^2 + (\sigma_{\text{corr2}})^2}{4}} \quad (3)$$

3.2. Procedural blanks and sample size

Extraction, purification and total procedural blank values are shown in Table 2. An additional combined reagent blank for sample acidification and subsequent pH adjustment was calculated to be $<0.03\text{ ng}$, based on published specifications from the manufacturer.

Table 3
Dissolved concentrations and stable isotope ratios for Fe, Zn and Cd in SAFe seawater standards. All isotope ratios are shown with $\pm 2\sigma$ error, and assumed error on concentrations is 2% (see text). SAFe consensus values are shown in parentheses.

Sample	[Fe] (nmol kg ⁻¹)	$\delta^{56}\text{Fe}$ (‰)	[Zn] (nmol kg ⁻¹)	$\delta^{66}\text{Zn}$ (‰)	[Cd] (pmol kg ⁻¹)	$\delta^{114}\text{Cd}$ (‰)
S1	0.097 (0.093 ± 0.008)	nd	0.08 (0.069 ± 0.01)	0.16 ± 0.14	0.84 (1.1 ± 0.3)	nd
D1 (321)	0.68 (0.67 ± 0.04)	-0.32 ± 0.09	7.64 (7.4 ± 0.35)	0.49 ± 0.03	982 (991 ± 31)	0.26 ± 0.04
D1 (329)	0.65 (0.67 ± 0.04)	-0.39 ± 0.12	7.67 (7.4 ± 0.35)	0.48 ± 0.03	983 (991 ± 31)	0.27 ± 0.04
D2 (494)	0.94 (0.933 ± 0.023)	-0.28 ± 0.07	7.56 (7.43 ± 0.25)	0.49 ± 0.03	970 (986 ± 23)	0.27 ± 0.04
D2 (501)	0.93 (0.933 ± 0.023)	-0.28 ± 0.07	7.60 (7.43 ± 0.25)	0.48 ± 0.03	968 (986 ± 23)	0.24 ± 0.04
D2 (64)	0.91 (0.933 ± 0.023)	-0.24 ± 0.05	7.51 (7.43 ± 0.25)	0.50 ± 0.02	969 (986 ± 23)	0.26 ± 0.04

Procedural blanks for Fe, Zn and Cd are lower than any previously published method; 0.3 ng for Fe c.f. 1.1–1.3 ng [29,30], 0.1 ng for Zn c.f. 13 ng [26] and 4 pg for Cd c.f. 20–30 pg [54].

On a single litre of seawater, $\delta^{56}\text{Fe}$ and $\delta^{66}\text{Zn}$ can reliably be determined for samples with concentrations as low as 0.1 nmol kg⁻¹ (6–7 ng) at <0.2‰ precision, with the precision for less concentrated samples depending on analytical sensitivity (see Fig. 3). For example, in the surface ocean where Zn may be <0.02 nmol kg⁻¹, samples were measured with 2σ errors of 0.2–0.4‰. This method allows determination with Cd as small as 0.5–1 ng of Cd (4–8 pmol L⁻¹) with 2σ error of 0.2–0.3‰. For Cd samples that are <5 pmol L⁻¹ (even sub-pmol L⁻¹) and Zn samples less than 200 pmol L⁻¹, concentrations which are observed in both the surface Atlantic and Pacific Oceans (Tables 3 and S-2), larger volumes are required. However, the quantitative recovery and low blanks of this technique mean that the processing could be easily adapted to larger sample volumes.

3.3. Extraction efficiency

Extraction efficiency of the method for Fe, Zn and Cd was determined by addition of standard to ‘metal-free’ seawater and

re-extraction. Extraction efficiencies for Cu, Co, Ni, Pb, and Mn were determined by extraction of four SAFe D1 and D2 standards (Mn on D2 only), and are expressed as a percentage of consensus values. Recovered metal concentrations were determined either by isotope dilution, or by comparison to concentration standards with standard addition to correct for matrix effects. Values are shown in Table 2, and demonstrate quantitative recovery for Zn and Cd and >80% recovery of Fe.

Extraction efficiencies for Fe, Zn and Cd were also determined during MC-ICPMS analysis of 47 North Atlantic seawater samples, which had been processed through the complete method described in Table 1. The amount of Fe, Zn or Cd extracted from each seawater sample was calculated using the measured MC-ICPMS voltage from each analysis, the volume of each final purified sample and the MC-ICPMS voltage measured in standards of known concentration. The extraction efficiency for each metal was then calculated by expressing the amount of metal extracted as a percentage of the amount of Fe, Zn or Cd in each original sample of seawater, as calculated by isotope-dilution (see Section 2.4.5). Extraction efficiencies in natural seawater samples were found to be $82 \pm 10\%$ for Fe and slightly less than quantitative for Zn ($80 \pm 7\%$) and Cd ($83 \pm 14\%$), based on signal intensity in purified samples. We tentatively ascribe

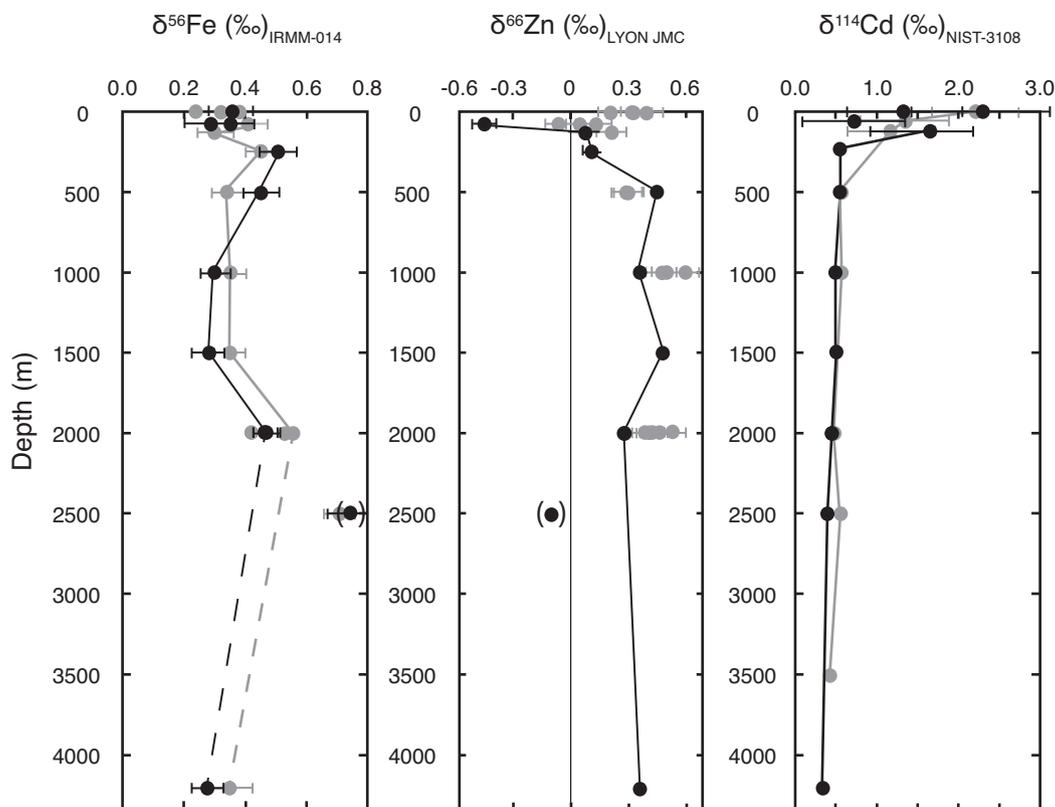


Fig. 5. Measured $\delta^{56}\text{Fe}$, $\delta^{66}\text{Zn}$ and $\delta^{114}\text{Cd}$ in samples from the GEOTRACES North Atlantic IC1 cruise (black points and lines are mean values from this study, grey points and lines from Boyle et al. [55]), with 2σ error bars shown where error is larger than the size of the point. Previously published $\delta^{114}\text{Cd}$ has been converted from $\varepsilon^{114}\text{Cd}$. The bracketed points are considered anomalous.

the lower apparent extraction efficiencies of Zn and Cd in North Atlantic seawater samples to matrix effects suppressing signal during MC-ICPMS analysis, but acknowledge that these reduced values could also point to slightly reduced Zn and Cd extraction efficiency in natural samples compared to seawater doped with metal.

3.4. Blanks and uncertainty on calculations of metal concentration

The calculated procedural blanks (Section 3.2) are equivalent to 5 pmol kg⁻¹ for Fe, 1 pmol kg⁻¹ for Zn and 35 fmol kg⁻¹ for Cd, and the standard deviation of two concentration analyses for a single sample is typically very small (<1%). We therefore believe that the largest source of error on these measurements is that associated with weighing and pipetting inaccuracy, which we conservatively estimate to be 2%. In order to establish the accuracy and precision of concentration measurements, SAFe standards (S, D1 and D2) were obtained from Ken Bruland (UC Santa Cruz) and processed as samples, with the results shown in Table 3; all values are in agreement with most recent consensus values (May 2013). Values are means of 2 (all S and Fe) or 4 (Zn and Cd; D1, D2) MC-ICPMS analyses. As an indicator of external precision, measurements are shown for separate extraction and analysis of two separate bottles of D1 and three separate bottles of D2.

3.5. GEOTRACES IC1 profile and SAFe samples

Dissolved $\delta^{114}\text{Cd}$, $\delta^{56}\text{Fe}$, $\delta^{66}\text{Zn}$ and metal concentrations were determined in samples obtained from the North Atlantic GEOTRACES IC1 cruise at the Bermuda Atlantic Time series site [55], using seawater previously sampled for $\delta^{56}\text{Fe}$ [37]. The results from these analyses are shown in Fig. 5 and Table S-2 (Supplementary Information), and for Fe and Cd demonstrate strong agreement with previously published values of both concentration and isotope ratio [37,54,55]. Zn concentration and isotope ratio are similar to previously published values [55], except at 75 m, where we observed a low Zn concentration (0.1 nmol kg⁻¹) and a very isotopically light $\delta^{66}\text{Zn}$ of -0.53% relative to previously published values (0.5 nmol kg⁻¹; -0.05 to 0.14%) [55]. However, the lower concentration of Zn reported here more-closely matches values of <0.2 nmol kg⁻¹ reported in other samples from this depth and location during the same cruise in 2008, and isotopically light excursions in $\delta^{66}\text{Zn}$ in the surface ocean have been previously reported, increasing our confidence in the data presented here [5,6]. We also obtained anomalously low concentrations of Fe and Zn at 2500 m, compared to expected values for the deep Atlantic. John and Adkins [37,55] also reported a lower than expected concentration for this sample, which may indicate that the $\delta^{56}\text{Fe}$ of $\sim 0.7\%$, reported by both this study and previous work [37,55], is not representative of the deep Atlantic at this point. Isotopic ratios for the SAFe concentration standards are shown in Table 3; we note the isotopically lighter values for $\delta^{56}\text{Fe}$ in these Pacific samples compared to those previously published for the North Atlantic [37,55], which suggest differences in the biogeochemical cycling of Fe between ocean basins.

4. Conclusions

A new method has been presented, using Nobias PA-1 chelating resin and double spike MC-ICPMS for the determination of three isotope systems ($\delta^{56}\text{Fe}$, $\delta^{66}\text{Zn}$ and $\delta^{114}\text{Cd}$), with high precision and accuracy, in a single 1 L sample of seawater. Low processing blanks (<0.03 ng), high extraction efficiency ($>80\%$) and the use of a double spike technique to correct for procedural and instrumental mass fractionation allow the generation of precise and accurate isotope

and concentration data over almost the complete range of expected Fe, Zn and Cd concentrations in natural seawater samples. Precision and accuracy have been evaluated by comparison to theoretical limits on analytical precision, by analysis of metal-free seawater doped with isotope standards, and by reference to the separation of internal isotope standards. We have also contributed to inter-calibration efforts with isotope and concentration data for SAFe samples and samples from the GEOTRACES IC1 cruise in the North Atlantic, where we show good agreement with previous measurements [55].

This method represents a significant improvement over previous studies, requiring 1–20 \times less volume per sample, whilst achieving lower blank contamination (4–130 \times lower). Simultaneous extraction and purification of the elements of interest also dramatically reduces the time and effort required for sample processing, when compared to previous studies utilizing coprecipitation and larger sample volumes for a single element. Because this is the first combined procedure for the analysis of Fe, Zn and Cd isotopes in seawater, and because this method requires only a single litre of seawater, it is optimal for high-resolution sampling and large-scale projects such as GEOTRACES, allowing for a more thorough investigation of the biogeochemical cycling of these important trace-metals in the ocean.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at <http://dx.doi.org/10.1016/j.aca.2013.07.025>.

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