Improvements to 232-thorium, 230-thorium, and 231-protactinium analysis in seawater arising from GEOTRACES intercalibration

Maureen E. Auro[1], Laura F. Robinson[1,2], Andrea Burke[1,3], Louisa I. Bradtmiller[1,4], Martin Q. Fleisher[5], and Robert F.Anderson[5]*

[1]Woods Hole Oceanographic Institution, 360 Woods Hole Road, Woods Hole, MA 02543 USA
[2]Department of Earth Sciences, University of Bristol, Bristol, UK
[3]Division of Geological and Planetary Sciences, California Institute of Technology, Pasadena, California, 91125 USA
[4]Environmental Studies Department, Macalester College, 1600 Grand Avenue, St. Paul, MN 55105 USA
[5]Lamont-Doherty Earth Observatory of Columbia University, P.O. Box 1000, Palisades, NY 10964 USA

Abstract

The GEOTRACES program requires the analysis of large numbers of seawater samples for ^{232}Th, ^{230}Th, and ^{231}Pa. During the GEOTRACES international intercalibration exercise, we encountered unexpected difficulties with recovery and contamination of these isotopes, ^{232}Th in particular. Experiments were carried out to identify the source of these issues, leading to a more streamlined and efficient procedure. The two particular problems that we identified and corrected were (1) frits in columns supplied by Bio-Rad Laboratories caused loss of Th during column chemistry and (2) new batches of AG1-X8 resin supplied by Bio-Rad Laboratories released more than 100 pg of ^{232}Th during elution of sample. To improve yields and blanks, we implemented a series of changes including switching to Eichrom anion exchange resin (100-200 μm mesh) and Environmental Express columns. All Th and Pa samples were analyzed on a Neptune multi-collector inductively-coupled-plasma mass spectrometer (MC-ICP-MS) using peak hopping of ^{230}Th and ^{229}Th on the central SEM, with either ^{232}Th, ^{236}U (or both) used to monitor for beam intensity. We used in-house laboratory standards to check for machine reproducibility, and the GEOTRACES intercalibration standard to check for accuracy. Over a 1-y period, the 2 s.d. reproducibility on the GEOTRACES SW STD 2010-1 was 2.5% for ^{230}Th, 1.8% for ^{232}Th, and 4% for ^{231}Pa. The lessons learned during this intercalibration process will be of value to those analyzing U-Th-Pa and rare earth elements as part of the GEOTRACES program as well as those using U-series elements in other applications that require high yields and low blanks, such as geochronology.

The international GEOTRACES program requires efficient, reproducible analyses of trace elements and isotopes in seawater (Geotraces Planning Group 2006). Given the many scientists participating in this effort, there are a large number of methods being used to measure each parameter. Chemical

*Corresponding author: E-mail: mauro@whoi.edu

procedures for measuring Th and Pa differ in detail, but broadly, spike isotopes (^{229}Th, ^{233}Pa) are added to the sample, the volume is reduced through coprecipitation (Fe[OH]$_3$, MnO$_2$ or Mg[OH]$_2$), and the sample is separated and purified using anion exchange chromatography before analysis (e.g., Chen et al. 1986). Early measurement methods on hundreds of liters of seawater used α-counting techniques to give a precision of 5% to 15% (e.g., Bacon and Anderson 1982; Nozaki and Yamada 1987). Sample size was reduced (~1 L) and precision improved (2%) for ^{232}Th analysis by using thermal ionization mass spectrometry (TIMS) methods (Chen et al. 1986). Developments in ICP-MS also allowed measurements to be made precisely. Single-collector-ICP-MS concentration measurements for ^{230}Th in seawater have been reported at 2% for 10-20 L deep water (Choi et al. 2001), MC-ICP-MS at 8% for 10 L samples (Robinson et al. 2004; Thomas et al. 2006), and ~1% to 20% on 1-2 L by TIMS (e.g., Moran et al. 1997; Moran et al. 2002).

This article documents recent developments and improvements made for analysis of ^{232}Th and ^{230}Th in seawater at the Woods Hole Oceanographic Institution (WHOI). At the outset of the GEOTRACES interlaboratory intercalibration exercise, we followed a procedure similar to that described in Chase et al. (2003). Although this method has previously been used to publish high-quality data (e.g., Chase et al. 2003), we were unable to produce results adequate to the requirements of the program where only 5 L seawater are available for analysis. The major problems that we encountered were low total chemical yield (~10%) and high and variable blanks. These two problems were particularly acute when analyzing waters from the uppermost water column where the concentrations of ^{230}Th and ^{231}Pa are the lowest.

In this article, we document the reasons why the previous method failed, the improvements we made, and describe in detail our modified chemical protocol. We also describe our analysis by Neptune MC-ICP-MS. During the chemical procedure we also separated and analyzed ^{231}Pa. The details of this method are only described in brief because the ^{231}Pa intercalibration effort is still in progress.

Materials and procedures

Sample preparation

In this section, we describe the steps that were taken to eliminate sources of contamination, and to improve chemical yield. The initial and final methods are compared side by side in Table 1 to highlight the major differences. In brief, both methods included spiking with ^{229}Th and ^{233}Pa, co-precipitation using Fe and purification using anion exchange chromatography.

Spike

Early experiments used a pure ^{229}Th spike from the California Institute of Technology (6.96×10^{-11} g/g). During the course of the intercalibration a new ^{229}Th spike was made. A concentrated ^{229}Th spike solution was calibrated by isotope dilution at WHOI with a ^{232}Th standard made by dissolution of ultra-pure ^{232}Th metal at the California Institute of Technology (Adkins Lab). This concentration was cross-checked by determining the ^{230}Th/^{238}U activity ratio of aliquots of Harwell Uraninite (HU-1) by isotope dilution with a mixed ^{236}U-^{229}Th spike (the ^{236}U concentration of which was calibrated by isotope dilution with the uranium concentration standard CRM-145). The measured ^{230}Th/^{238}U activity ratio of the HU-1 aliquots gave a value within error of secular equilibrium (Burke and Robinson 2012). A gravimetric dilution of the concentrated ^{229}Th solution was made for analysis of water samples (^{229}Th concentration of 6.48 pg/g ± 1.25×10^{-2} with minor contributions of ^{232}Th at 0.1 pg/g and ^{230}Th at 0.3 fg/g). A total of 3 pg of ^{229}Th were added to each sample. The ^{233}Pa spike was prepared from the irradiation of approximately 30 mg thorium nitrate (Th[NO$_3$]$_4$·H$_2$O) pressed into a Nuclepore filter. The irradiation took place at the Massachusetts Institute of Technology nuclear reactor (Anderson and Fleer 1982). The target material was irradiated at 4.9 MWt for 1440 min, resulting in ^{233}Pa activity of 1.4-1.6 mCi. We followed the protocol of Anderson and Fleer (1982) for ^{233}Pa purification with minor modifications such as using Bio-Rad AG1-X8 anion exchange resin. Separation of ^{233}Pa from ^{231}Pa and ^{232}Th was adequate, as shown by the final blank levels in the full chemical procedure for a typical seawater sample (as low as 0.2 fg ^{231}Pa, 0.2 fg ^{230}Th, and 4.5 pg ^{232}Th).

Initial method

In our initial method, the samples were obtained in 10 L Hedwin brand cubitainers. Cubitainers, and all other plastics except Teflon® were cleaned using 10% HCl (reagent grade (RG); Fisher Scientific) for at least 48 h, rinsed three times with 18.2 MΩ high-purity water (Milli-Q® Element, Millipore), then soaked in Milli-Q® water for 24 h and rinsed with Milli-Q® one final time before use. All Teflon® (Savillex Corp.) was cleaned in 1 L Teflon® jars by heating on a hotplate at 200°C in 8N HNO$_3$ (RG) for at least 24 h, rinsing 3 times with Milli-Q® water, heating in 6N HCl (RG) for another 24 h and rinsing again three times in Milli-Q® water. Finally, each vial was filled one quarter full of 16N HNO$_3$ (Optima grade (OG); Fisher Scientific), capped tightly and refluxed for at least 4 h on a hotplate at 200°C, and rinsed three times in Milli-Q® water before use.

Each seawater sample (10 L) was spiked with ^{229}Th and ^{233}Pa and left to equilibrate for at least 24 h. An aliquot of 1.5 mL (20 mg/1 mL) of Fe dissolved in 4N HCl (OG) was added to each sample and then Fe-precipitation was induced straight away by adding ammonium hydroxide (OG, Fisher Scientific) to achieve a pH between 8 and 9. Each cubitainer was shaken multiple times throughout the first day of precipitation to promote scavenging of Th and Pa onto the precipitate, and then the cubitainers rested for an additional 48 h. The cubitainer was fitted with an acid-cleaned spigot, turned upside-down and the precipitate left to settle out for at least 24 h. The Fe-precipitate was removed from the cubitainer using the spigot and collected in a 500 mL centrifuge tube (Corning). Each tube was centrifuged at 3500 rpm for 10 min, the supernatant removed, and the pellet rinsed with approximately 15 mL of pH 8 Milli-Q® water (made using ammonium hydroxide, OG) three times. This centrifuge and rinse procedure was repeated a total of three times to ensure removal of any salt matrix. The pellet was dissolved with a minimum amount of 12N HCl (OG), and transferred into a 50 mL polypropylene centrifuge tube (Fisherbrand), and the volume brought up to 40 mL with Milli-Q® water. The samples were then reprecipitated, centrifuged, decanted, and rinsed/centrifuged two more times with pH 8 Milli-Q® water to further remove any salt matrix. The pellet was redissolved in 1 mL 16N HNO$_3$ (OG) and transferred to a 30 mL Teflon® vial. The centrifuge tube was rinsed twice with 1 mL 16N HNO$_3$ (OG), and the rinse was added to the vial along with 1 mL 12N HCl (OG) to help remove organic material. The vials were heated at 200°C, then 250 μL 29N HF (OG) was added and heated to fumes twice to remove amorphous silicon. The walls of the

Table 1. Comparison of sample preparation before and after improvements.

Original method	New method
Spike samples with Th and Pa; equilibrate for at least 1 d	As original
Add approximately 30 mg Fe, coprecipitate using NH_4OH to bring the seawater to a pH between 8 and 9	Add approximately 100 mg Fe, coprecipitate using NH_4OH to bring the seawater to a pH between 7.5 and 8
Collect precipitate in 500 mL centrifuge tube (acid cleaned), centrifuge, rinse pellet with pH 8 Milli-Q® H_2O, decant, repeat a total of 3 times	Collect precipitate in 500 mL centrifuge tube (acid cleaned), centrifuge, and remove supernatant
Dissolve precipitate in a minimum amount of 12N HCl (OG), transfer to 50 mL polypropylene centrifuge tube, bring up to 40 mL w/ Milli-Q® H_2O, re-precipitate, centrifuge, rinse, decant, repeat 2 more times with pH 8 Milli-Q® H_2O	
	Resuspend pellet in small volume of pH 8 Milli-Q® H_2O and transfer to a 50 mL Teflon® centrifuge tube
Dissolve precipitate in 1mL 16N HNO_3 (OG), transfer to 30 mL Teflon® vial, rinse centrifuge tube 2 times with 1 mL 16N HNO_3 (OG) and add to vial along with 1 mL 12N HCl (OG)	Rinse pellet 3 times with pH 8 Milli-Q® H_2O; centrifuge and decant between each rinse
Heat samples at 200°C, add 250 μL HF, heat to fumes, repeat HF addition	
Rinse walls of vial with 1-2 mL 16N HNO_3 (OG), heat down to tiny volume	
Add 1N HCl (OG), transfer back to centrifuge tube, reprecipitate, centrifuge, decant, repeat 2 times, decant	
Initial column to separate Th and Pa	
Use 5 mL Bio-Rad AG1-X8 resin in Bio-Rad columns	Use 0.5 mL Eichrom prefilter resin, then 1-X8 resin in Environmental Express columns
Clean and condition columns with 2 × 5mL 12N HCl 0.13N HF (RG), 2 × 10 mL Milli-Q® H_2O, 10 mL12N HCl (RG), 10 mL Milli-Q® H_2O, 10 mL 8N HNO_3 (RG), 10 mL Milli-Q® H_2O, 2 × 5 mL 12N HCl (OG)	Clean and condition columns with 2 × 5 mL 12N HCl + 0.13N HF (RG), 2 × 10 mL Milli-Q® H_2O, 2 × 5 mL12N HCl (OG)
Dissolve samples in 10 mL 12N HCl (OG), load onto columns with Teflon® vial for eluent	As original
Rinse the centrifuge tube with 2 × 2 mL 12N HCl (OG), load, wash with 3 × 5 mL 12N HCl (OG)	As original
Add 1 mL 16N HNO_3 (OG) to vial, dry down at 100°C	As original
Add 3 × 5 mL 12N HCl + 0.13N HF (OG) to elute Pa	As original
Th "Clean-up" column	
Use 2 mL Bio-Rad AG1-X8 resin in Bio-Rad columns	Use 0.5 mL Eichrom pre-filter resin then 2 mL Eichrom 1-X8 resin in Environmental Express columns
Clean and condition with 5 mL 12N HCl (RG), 10 mL Milli-Q® H_2O, 10 mL 7.5N HNO_3 (RG), 10 mL Milli-Q® H_2O, 2 × 4 mL 8N HNO_3 (OG)	Clean and condition with 5 mL 12N HCl (RG), 10 mL Milli-Q® H_2O, 2 × 4 mL 8N HNO_3 (OG)
Heat the samples down to a small volume of HCl.	As original
Add a few milliliters of 16N HNO_3 (OG) and heat down. Repeat several times to ensure that all the HCl is driven off	As original
Heat the HNO_3 to about 0.5 mL. Add 0.5 mL Milli-Q® H_2O and let cool	As original
Add 3 mL 8N HNO_3 (OG) to each sample vial and load onto columns	As original
Rinse vials with 2 mL 8N HNO_3 (OG), load onto the columns	As original
Wash resin with 2 × 2 mL 8N HNO_3 (OG) and then 200 μL 12N HCl (OG)	As original
Elute Th with 4 × 3 mL 12N HCl (OG), dry down at 200°C	As original
Pa "Clean-up" column	
Use 1 mL Bio-Rad AG1-X8 resin in Bio-Rad columns	Use 0.5 mL Eichrom pre-filter resin, then 1.5 mL Eichrom 1-X8 resin in Environmental Express columns
Add a few drops of 16N HNO_3 (OG) to each sample, heat to fumes, add 1 mL 12N HCl (OG) and heat to a droplet. Cool. Add 2 drops 12N HCl (OG), then 2 mL 12N HCl (OG)	As original
Condition columns with 4 mL 12N HCl + 0.13N HF (RG), 10 mL Milli-Q® H_2O, 10 mL 12N HCl (RG), 10 mL Milli-Q® H_2O, and 2 × 2 mL 12N HCl (OG)	As original
Load samples onto columns. Rinse vials with 2 × 2 mL 12N HCl (No HF), load onto columns	As original
Rinse with 3 × 2 mL 12N HCl (OG)	As original
Elute Pa with 3 × 2 mL 12N HCl + 0.13N HF (OG). Record time/date. Dry down at 200°C.	As original

beaker were rinsed with 1-2 mL 16N HNO$_3$ (OG) and heated down to a small viscous bead. Each sample was redissolved in 0.5 mL 12N HCl (OG), 5.5 mL Milli-Q® H$_2$O was added, and the solution transferred back to the 50 mL centrifuge tubes, reprecipitated to remove any residual salts, centrifuged, and decanted. This procedure was repeated two more times. Samples were dissolved in 10 mL of 12N HCl (OG).

Three separate columns were used for the separation of Th and Pa; the first column was for removing the Fe and the other two columns as final "clean-up." The first column (Poly-Prep, Bio-Rad Laboratories) contained 5 mL AG1-X8 resin (hand-packed, 100-200 μm mesh; Bio-Rad Laboratories). This volume of resin was required to remove all of the iron. Each column was cleaned as follows: 2 × 5 mL 12N HCl (OG), 2 × 5 mL 12N HCl + 0.13N HF (RG), 2 × 10 mL Milli-Q® H$_2$O, 10 mL 12N HCl (RG), 10 mL Milli-Q® H$_2$O, 10 mL 8N HNO$_3$ (RG), 10 mL Milli-Q® H$_2$O, and finally 2 × 5 mL 12N HCl (OG). The samples were loaded in 12N HCl (OG) and the effluent, containing Th, was collected in Teflon® vials. The centrifuge tube was rinsed with 2 × 2 mL 12N HCl (OG), each rinse was loaded onto the columns, and then an additional 3 × 5 mL 12N HCl (OG) was used to complete the elution. Solutions containing Th were dried at 100°C with the addition of 1 mL 16N HNO$_3$ (OG) until only a small volume remained. Following elution of Th, Pa was eluted into clean 30 mL Teflon® vials with 3 × 5 mL 12N HCl + 0.13N HF (OG) and dried to a small volume with the addition of 1 mL 16N HNO$_3$ (OG).

The Th "clean-up" columns were Poly-Prep columns hand-packed with 2 mL AG1-X8 resin (Bio-Rad Laboratories) that was cleaned with 5 mL 12N HCl (RG), 10 mL Milli-Q® H$_2$O, 10 mL 7.5N HNO$_3$ (RG), 10 mL Milli-Q® H$_2$O, and conditioned in 2 × 4 mL 8N HNO$_3$ (OG). The samples were converted to HNO$_3$, and a total of 4 mL 8N HNO$_3$ (OG) was added to each sample before loading onto the column. After loading, the sample vials were rinsed with 2 mL 8N HNO$_3$ (OG), and this rinse was also loaded onto the columns. The columns were washed with 2 × 2 mL 8N HNO$_3$ (OG) and then with 200 μL 12N HCl (OG). The Th fraction was eluted with 4 × 3 mL 12N HCl (OG) into 30 mL Teflon® vials, and then dried down on a hotplate at 200°C.

The Pa "clean-up" columns were new Poly-Prep columns that were hand-packed with 1 mL AG1-X8 resin (Bio-Rad Laboratories). These columns were cleaned with 4 mL 12N HCl + 0.13N HF (RG), 10 mL Milli-Q® H$_2$O, 4 mL 12N HCl (RG), 10 mL Milli-Q® H$_2$O, 4 mL 12N HCl (RG), 10 mL Milli-Q® H$_2$O, and conditioned with 2 × 2 mL 12N HCl (OG). Samples were dried down to a droplet, 1 mL 12N HCl (OG) was added to each sample, dried down to a droplet again, then 2 mL 12N HCl (OG) was added in final preparation for sample loading. Samples were loaded onto columns, vials were rinsed with 2 × 2 mL 12N HCl (OG), loaded onto columns, and the resin was rinsed with 3 × 2 mL 12N HCl (OG). Pa was eluted with 3 × 2 mL 12N HCl + 0.13N HF (OG) into 30 mL Teflon® vials, and then dried down on a hotplate at 200°C.

Yield

We used a [232]Th standard to monitor chemical yield through precipitation and column chemistry, and determined that our initial protocol produced a yield less than 10%. Most of the Th loss occurred during the column chemistry (columns alone gave a 23% yield). After testing each step of the chemical procedure (batches of resin, acid strengths, elution calibration, column brands, and varying amounts of Fe), we established that the losses were being caused by the frits in the Bio-Rad columns. The same brand of columns had been used for similar chemical procedures in the past with a higher recovery. Personal correspondence with technical chemists at Eichrom Technologies revealed that some frits are treated with a surfactant that aids in the dripping of the columns, but it has been found to cause binding of elements as well. The decrease in recovery may indicate that there had been a change in the manufacturing protocol of the frits. Switching to Environmental Express columns (Cat. #R1010) instantly increased our yield from 23% to 92% with no other change in the column chemistry. We also established that there was some loss in recovery during the precipitation step. To improve this recovery, we varied the amount of iron used for the coprecipitation and found that ~100 mg Fe in solution gave the best recovery and also checked that pH during precipitation did not go above 9. In addition, our use of the spigot for draining the Fe coprecipitation was not ideal, and left a residue of orange precipitate on the sides of the cubitainer that could not be removed. To address this problem, we removed the excess liquid in each cubitainer from the top using a peristaltic pump with L/S 24 tubing (Masterflex Tygon) fitted with a 12-inch piece of acid-cleaned Teflon® tubing. An alternative to pumping is to siphon off the liquid.

Contamination

In our early tests, we found [232]Th chemical blanks up to 100 pg, similar to the amount of [232]Th in liter-sized seawater samples (Fig. 1). Clearly this level of contamination renders
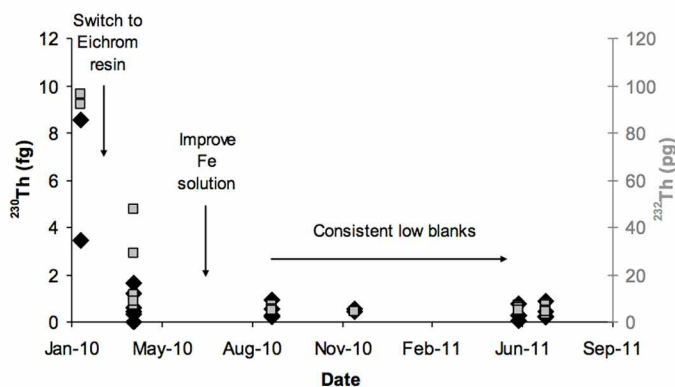

Fig. 1. Background contamination levels were high at the outset of the intercalibration effort, with a large proportion of the contamination coming from the resin (see Fig. 2). Black symbols represent [230]Th, and gray symbols represent [232]Th.
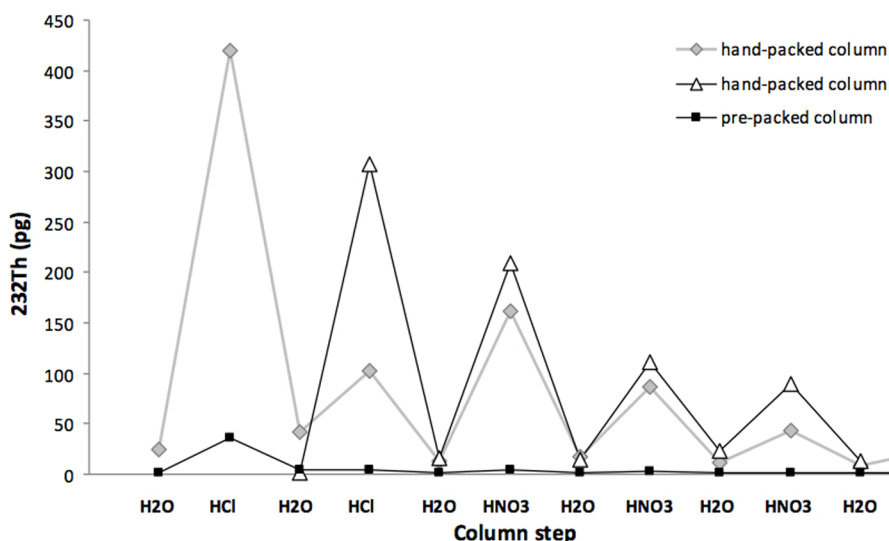
Fig. 2. Results of column test to determine contamination from resin. The columns were 10 mL Bio-Rad columns with 2 mL resin, and reagent volumes were 10 mL each. The reagent was collected after each step of the column procedure and its ^{232}Th content analyzed. Prepacked columns appeared to be less contaminated. Acid strengths were 6N HCl and 8N HNO$_3$. The gray diamond has a longer cleaning protocol compared with the open triangle.

the data unusable and so a series of tests were undertaken to identify and eliminate the sources of contamination. At the same time, we noted a significant increase in ^{232}Th and ^{238}U blanks using a similar protocol for recovery of U-Th-Pa from carbonate materials. The carbonate and seawater samples were being processed in separate laboratories to ensure no cross contamination between carbonate and seawater samples. First we re-examined the column chemistry, and discovered that significant amounts of ^{232}Th were being eluted off the resin during both rinsing and elution steps (Fig. 2). We checked (a) resin straight from the bottle to assess whether our prior cleaning had introduced contamination, (b) resin from a new bottle, (c) resin from both labs, and (d) resin from pre-packed Bio-Rad columns. Each test gave similarly high levels of contamination except the pre-packed columns, which had blanks as low as 1.5pg. We suspect that these pre-packed columns may have been made up from earlier batches of Bio-Rad AG1-X8 resin that did not exhibit the high contamination levels. Our first strategy was to add additional cleaning steps to the column protocol. Despite reducing the blanks to more acceptable levels, the procedure was time consuming, and increased the length of the chemical purification from approximately 2 h to 4 h. Instead, we purchased an equivalent resin from Eichrom Technologies and found that the ^{232}Th (and ^{238}U) levels were at the picogram level after the original cleaning procedure.

We made our original Fe solution by dissolving ultra-pure Fe ribbon in a combination of HCl and HNO$_3$. The dissolution protocol produced a clean Fe solution, but only small quantities could be made because of the vigorous reaction. Instead we used an iron solution purified through repeated extraction into isopropyl ether. First we dissolved Fe(III) chloride (Acros

Organics) pellets (~50 g) in approximately 75 mL of 8.2N HCl (OG) in a Teflon® jar. Using a glass separating funnel, we cleaned anhydrous ether (~50 mL; Acros Organics, certified ACS) using 10-15 mL ~8N HCl (OG), shaking and degassing to mix the two thoroughly. The mixture was allowed to settle for a few minutes and the HCl and ether separated. Once the ether was clean and the HCl was removed, 30 mL portions of the Fe solution were added to the ether in the funnel, and repeat shaking/degassing was performed. After waiting for a clear separation between the waste HCl and the ether/Fe mixture, the waste acid was drained off and re-extraction of the Fe solution was done by adding water. The Fe in the water was collected in a clean Teflon® vial. The clean Fe solution was dried down and the Fe residue was redissolved in 4N HCl (OG). However, we found that the resulting Fe solution was not sufficiently clean, giving ^{232}Th blanks of ~30 pg (Fig. 1). The blank could be reduced by passing the Fe solution through a clean-up column to remove the ^{232}Th. Whereas this method was effective at producing Fe with ^{232}Th < 1 pg per aliquot the quantities of Fe produced were small. Instead we repeated the ether extraction (with the insufficiently clean Fe from above) which produced a clean Fe solution of 97 mg/mL, which was used for all subsequent samples.

Our final significant improvement to the procedural blank came from replacing the acid cleaned Fisherbrand 50 mL polypropylene tubes with Savillex Corp. Teflon®. Together these improvements gave an average background contamination for the complete chemical procedure of 7.0 ± 0.9 pg for ^{232}Th and 0.6 ± 0.9 fg for ^{230}Th (*n* = 14 over 11 months) (Fig. 1).

New method

Here we summarize the improved method for chemical preparation of seawater samples. The new method provides

more reproducible, low blank results and is less time consuming than the initial method. Samples (5 L) were spiked with ^{229}Th and ^{233}Pa, set aside to equilibrate for at least 24 h, then 1 mL of the FeCl$_3$ solution (97 mg Fe/sample) was added to each sample and precipitated with ammonium hydroxide (OG) to a pH range between 7.5-8 and set aside for 1 week. Using a MasterFlex LS EasyLoad peristaltic pump fitted with L/S 24 tubing (Masterflex Tygon) and a 12-inch piece of acid-cleaned Teflon® tubing on the end, the seawater supernatant was removed from each cubitainer. The Teflon® tubing was the only piece inserted directly into the sample. Adjustments were made to the speed of the peristaltic pump throughout the supernatant removal to remove as much seawater as possible without disturbing the precipitate. Speeds ranged from 500 to 100 mL/min. When less than 500 mL were left in each cubitainer, it was poured into 500 mL centrifuge tubes. Each cubitainer was rinsed three times with a small volume of pH 8 Milli-Q® H$_2$O to recover any remaining residue and added to the appropriate centrifuge tubes. The samples were then spun down to a pellet, and supernatant decanted. The sample pellets were dislodged with a small amount of pH 8 Milli-Q® H$_2$O and transferred into the clean 50 mL Teflon® centrifuge tubes. Transfer of the sample pellet from the 500 mL tubes to the 50 mL tubes was performed before dissolution in 12N HCl (OG) since the 500 mL polypropylene tubes proved to be a source of contamination if exposed to concentrated acid. The 500 mL tubes were rinsed until all precipitate was transferred to the 50 mL tube using pH 8 Milli-Q® H$_2$O. Samples were then centrifuged for 10 min at 3500 rpm, decanted, rinsed with pH 8 Milli-Q® H$_2$O, centrifuged (repeated three times), and dissolved in 10 mL 12N HCl (OG). The digestion step using HF was removed in the new method since GEOTRACES dissolved samples are prefiltered with a 0.45 µm Acropak capsule so Th and Pa binding silicates would have been removed from each sample, removing the need to break apart silicates to release any Th or Pa incorporated in them. It may, however, be advisable to add HF when processing high Si water samples to remove any amorphous silicon.

Each acid-cleaned Environmental Express column was loaded with 0.5 mL pre-filter resin (Eichrom Technolgies) and then topped off with 5 mL Anion Exchange Resin (1-X8, 100-200 mesh; Eichrom Technologies). The prefilter resin was used to aid in removal of organics to alleviate clogging during mass spectrometry. The columns were conditioned with 2 × 5 mL 12N HCl + 0.13N HF (RG), 2 × 10 mL Milli-Q® H$_2$O, then 2 × 5 mL 12N HCl (OG). The samples were loaded onto the columns, centrifuge tubes were rinsed with 2 × 2 mL 12N HCl (OG), and each rinse was loaded onto the columns. The columns were washed with 3 × 5 mL 12N HCl (OG), and the Th was eluted into 30 mL Teflon® vials. Nd and other rare earth elements (REE) are carried with Th to this point, and they may be separated from Th as described below if so desired. Concentrated HNO$_3$ (OG, 1 mL) was added to each sample before drying down, and samples were dried to a droplet at 100°C and converted to nitric form. Protactinium was eluted and collected into 30 mL Teflon® vials with 3 × 5 mL 12N HCl + 0.13N HF (OG).

Final samples for Th column loading were in 4 mL 8N HNO$_3$ (OG). Thorium "clean-up" columns were new, acid-cleaned Environmental Express columns hand-packed with 0.5 mL pre-filter resin (Eichrom Technologies) and 2 mL 1-X8 Anion Exchange Resin (100-200 µm mesh, Eichrom Technologies). The columns were cleaned with 5 mL 12N HCl (RG), 10 mL Milli-Q® H$_2$O, and conditioned with 2 × 4 mL 8N HNO$_3$ (OG). Samples were loaded in their nitric form, vials rinsed with 2 mL 8N HNO$_3$ (OG) and loaded onto the columns, and then the columns were washed with 2 × 2 mL 8N HNO$_3$ (OG). A small volume (200 µL) of 12N HCl (OG) was added to each column to bring the Th toward the column tip. At this point, the Nd and other REE have eluted with the 8N HNO$_3$, which should be collected if the analysis of Nd isotope ratios or REE concentrations is desired. Thorium was eluted (into the previously used Th vials) with 4 × 3 mL 12N HCl (OG). Th yield through columns was greater than 90%. Each sample was spiked with 20 µL ^{236}U (~1.7 ppb) after elution from the above column to improve mass spectrometry (see below).

The Pa fraction from the initial column was dried to a small volume and dissolved in 12N HCl (OG) before Pa "clean-up" chemistry. Protactinium "clean-up" columns were new, acid-cleaned Environmental Express columns hand-packed with 0.5 mL prefilter resin (Eichrom Technologies) and 1.5 mL 1-X8 Anion Exchange Resin (100-200 µm mesh, Eichrom Technologies). Columns were cleaned with 4 mL 12N HCl + 0.13N HF (RG), 10 mL Milli-Q® H$_2$O, 10 mL 12N HCl (RG), 10 mL Milli-Q® H$_2$O, and then conditioned with 2 × 2 mL 12N HCl (OG). Samples were loaded, and vials were rinsed with 2 × 2 mL 12N HCl (OG; No HF), loaded onto columns and columns were rinsed with 3 × 2 mL 12N HCl (OG). Protactinium was eluted with 3 × 2 mL 12N HCl + 0.13N HF (OG), and the date and time of elution was recorded. Pa yield through columns was close to 100%. Samples were spiked with 20 µL ^{236}U (~1.7 ppb) after column chemistry to quantify possible leakage of uranium through the columns, and dried down. The new method from the start of spiking to the end of column chemistry takes 10 d, saving at least 2 d from the initial protocol.

Calibration of the ^{233}Pa spike for this study was performed in two ways. First, after the ^{233}Pa spike was fully decayed (typically after 6 months, > 5 half lives), we spiked aliquots of the decayed spike with a known concentration of ^{233}U and performed a ^{236}U/^{233}U analysis on the MC-ICP-MS. We used this ratio to calculate the total amount of ^{233}U which is equal to the total initial ^{233}Pa concentration. Second, to avoid the lag time involved in this final calibration process, we made an in-house ^{231}Pa standard that could be analyzed with each batch of samples to provide an immediate calibration of the spike. This ^{231}Pa was calibrated using ^{233}Pa spike calibrated as above (i.e., with ^{236}U, after full decay).

Mass spectrometry

All analyses were made in the WHOI plasma facility using a Neptune MC-ICP-MS, which was retrofitted with a four-counter multi-ion-counter (MIC) array optimized for analysis of low level thorium and protactinium. The array was designed to allow ^{229}Th, ^{230}Th, and ^{232}Th to be analyzed concurrently (^{232}Th on a Faraday cup) and to allow ^{231}Pa and ^{233}Pa to be analyzed concurrently in a separate run (Fig. 3). For the reasons outlined below, the final protocol only used the MIC array for Pa analysis, and Th was analyzed on the central Secondary Electron Multiplier (SEM) in a two-step procedure. In all cases, samples were introduced via a CETAC Aridus 1 desolvating nebulizer, and samples were run in 5% HNO_3 (OG) with 0.13N HF. Typical sensitivity was about 5 volts for a 10 ppb uranium solution with an uptake rate of about 100 µL/min representing an ionization efficiency of nearly 1%.

Thorium

Initially Th was analyzed using the MIC array because concurrent analysis of all Th isotopes improves the counting statistics, and because the ratios should have a higher precision since beam instability does not affect the ratio. The ^{232}Th beam was analyzed in Faraday cup L3, ^{230}Th in IC5, and ^{229}Th in IC4, and a second, shorter step was included to assess peak tailing at half masses in IC5, IC4, and IC3. Machine biases were assessed using the uranium standard CRM-145, and the accuracy of the method was assessed using an in-house Th standard that was previously made and calibrated at the California Institute of Technology (Th-SGS, Robinson et al. 2005). However, we found that counting statistics were not our limiting factor once we had improved our chemical yield. The MIC array requires a lengthy set up, and the counters in the MIC array have a relatively short life span compared to the SEM, so the counting efficiency drifts during the run. Additionally, the dark noise was high on IC5 because of the use of a ^{233}Pa spike (see below). For these reasons, we decided to switch to an alternative two-step method for analyzing thorium, leaving the MIC array dedicated to analysis of low levels of protactinium.

The new method for analyzing thorium was a 'peak-hopping' method where ^{229}Th and ^{230}Th were each analyzed on the central SEM for 4.2 s, and the steps were cycled 40 times. The ^{232}Th beam was analyzed in both steps, allowing direct determination of ^{232}Th/^{230}Th and ^{232}Th/^{229}Th. The ratio ^{230}Th/^{229}Th could then be calculated directly, or from the two former ratios, thus accounting for beam instability and typically improving precision if the beam signal became unstable. As a final check, we also added ^{236}U to each sample after column chemistry and analyzed ^{236}U in each step so that ^{230}Th/^{229}Th could be calculated using (^{230}Th/^{236}U)/(^{229}Th/^{236}U). This approach gave us three different ways of calculating ^{230}Th/^{229}Th. In this intercalibration study, we always used the ratio calculated directly, and the agreement between the three methods was used as a monitor on the performance of the method (Fig. 4). Accuracy was assessed using a secondary consistency standard made at WHOI from ^{229}Th, ^{230}Th, and ^{232}Th solutions (ThB, Fig. 4). The concentration of the standard is not well known, but the ratios were determined precisely by analyzing them on Faraday cups and using ^{235}U/^{238}U in CRM-145 in bracketing standards to assess mass bias. The final ratios of ThB and 2 s.d. uncertainties were ^{232}Th/^{230}Th = 293.03 ± 0.06, ^{232}Th/^{229}Th = 239.87 ± 0.02, and ^{230}Th /^{229}Th = 0.8186 ± 0.0002. Over the time period of June 2010-July 2011, ThB was run 26 times with GEOTRACES samples and the ^{232}Th/^{229}Th and ^{230}Th/^{229}Th of all of these analyses are shown in Fig. 4. For each of the methods of calculating the ^{230}Th /^{229}Th, the average offset was –0.7‰ for ^{236}U normalized methods, 0.4‰ for the direct method, and 0.7‰ for the ^{232}Th normalized method. The average offset for the ^{232}Th/^{229}Th ratio from the true ratio was –3.0‰. The largest offsets were in June 2010 and September 2010, but the offsets became smaller when the Th-SGS was rediluted, and we concluded that the earlier Th-SGS dilution had become contaminated with ^{232}Th. ThB was also run with other samples (for geochronology) during the same time period, with an overall reproducibility of 1.7‰ for ^{230}Th/^{229}Th, 3.8‰ for ^{232}Th/^{230}Th, and 4.2‰ for ^{232}Th/^{229}Th. In

	Step	time	IC3	IC4	IC5	L4	L3	L2	L1	C (SEM)	H1	H2	H3	H4
Thorium	1	4.2s								^{230}Th	^{232}Th		^{236}U	
	2	4.2s								^{229}Th		^{232}Th		^{236}U
Uranium	1	4.2s			^{234}U	^{235}U		^{238}U						
	2	4.2s		^{234}U		^{236}U	^{238}U							
	3	4.2s	^{234}U											
Protactinium	1	8.4s	^{231}Pa		^{233}Pa		^{236}U		^{238}U					
	2	1.2s	230.5	231.5	232.5									

Fig. 3. Collector array used for analysis of Th and Pa in seawater. IC3, IC4, and IC5 are channeltron ion counters, which are attached to L4. L4-L1 and H4-H1 are Faradays, and the central cup was used as an SEM.
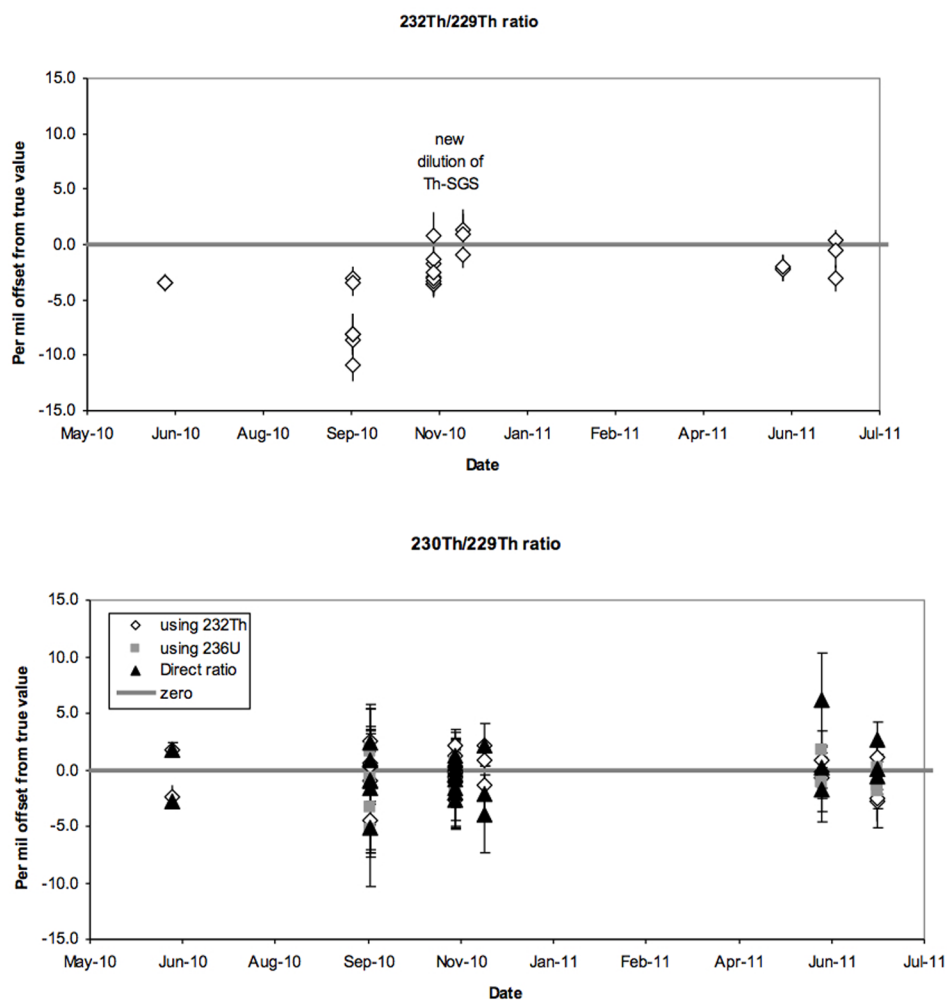
Fig. 4. Repeat analysis of ThB in-house Th standard over 1 y, showing ‰ offset from the predetermined value. These ratios were corrected for machine blank, then a linear correction for machine biases applied by direct comparison to the TH-SGS standard. All analyses shown here were measured with GEOTRACES samples or standards. ThB was analyzed on other dates during this time period, but with other sample types. Errors are the standard error of 30 cycles of 4.2 s.

the geochronology analyses, the ^{230}Th/^{229}Th ratio was the focus and ^{232}Th/^{229}Th exhibited more scatter than for the ThB analyses made with the GEOTRACES SW STD 2010-1 standard, again most likely due to ^{232}Th contamination in the Th-SGS. A typical run included ThB at the beginning and after every 4 samples (Table 2). The Th-SGS was run between every two samples, and an acid wash test was run between every sample and standard (Table 2). For a set of 12 seawater samples, we analyzed two full procedural blanks, two SW STD 2010-1 standards (Anderson et al. 2012) with chemistry performed in cubitainers and seven ThB mass spectrometric standards.

Data reduction was straightforward and included (a) subtraction of machine background using bracketing, (b) correction for peak tailing from ^{232}Th on ^{230}Th and ^{229}Th, (c) linear correction for machine biases using bracketing Th-SGS samples, which includes both SEM yield and mass bias, (d) sub-

traction of full procedural blank, and (e) calculation of ^{230}Th and ^{232}Th concentrations using the ^{229}Th concentration of spike. We considered various methods for assessing peak tailing for ^{232}Th onto ^{230}Th and ^{229}Th. The Th-SGS standard had a ^{232}Th/^{230}Th ratio of 125, lower than seawater samples that can vary from typical deep water values of 1000-5000 up to surface water values of more than 50,000 (e.g., Moran et al. 2002). The abundance sensitivity determined using U and Th standards at two mass units is approximately 1 ppm, and at three mass units is approximately 0.5 ppm of the beam intensity. In the most extreme case, not accounting for this peak tailing would lead to an overestimate of the ^{230}Th concentration of 0.05% at a ratio of 1000, 0.5% at 10,000, and 5% at 100,000. The GEOTRACES SW STD 2010-1 Th-Pa standard has a ratio close to ~4000, so peak tailing effects could lead to a 0.2% offset from the true value. For seawater samples, we made a peak tailing correction from ^{232}Th of 0.5 ppm to ^{229}Th and 1 ppm to ^{230}Th

Table 2. Typical run sequence for Th analysis.

Solution	Rinse time (mins)	Cycles number
ThSGS	3	30
Acid blank	6	10
ThB	1	30
ThSGS	4	30
Acid blank	6	10
Sample	1	40
Acid blank	4	10
Sample	1	40
Acid blank	4	10
ThSGS	1	30
Acid blank	6	10
Sample	1	40
Acid blank	4	10
Sample	1	40
Acid blank	4	10
ThSGS	1	30
Acid blank	6	10
ThB	1	30
ThSGS	4	30

(using the values derived above) before calculating the ^{230}Th concentration and final ^{232}Th/^{230}Th ratios. We did not propagate an uncertainty associated with this correction, but it is expected to be small relative to other uncertainties based on the relative size of the correction (up to a maximum of about 5% in surface waters) and the constant shape of the peak tail.

Protactinium

Since the concentration of Pa in seawater is very low (less than 4 fg/kg depending on water depth), optimizing the number of detected counts was a primary concern, so the MIC array was used for concurrent analysis of ^{231}Pa and ^{233}Pa. First the yield of each ion counter was calibrated using the mass bias corrected ^{234}U/^{238}U ratio of CRM-145 uranium standard, with the ^{234}U in the ion counter and the ^{238}U in a Faraday cup (Fig. 3). Due to inflexibility of the Neptune array, the ^{238}U could not be measured at the same time as ^{234}U on IC3, so the yield for this ion counter had to be calculated using the ^{238}U intensity from the average of the two adjacent steps. This approach was satisfactory as long as the beam was stable, and typically gave an uncertainty of the ratio of less than 0.4% 2 s.e. over 15 cycles of 4.2 s for IC3. Mass bias was monitored using the ^{238}U/^{235}U ratio measured in two Faraday cups. A CRM-145 bracketing standard was analyzed between every two samples and drift monitored throughout the run. For analysis of each sample, we used a two-step routine with 40 cycles. In the first step, ^{236}U was analyzed in faraday cup L3, ^{238}U in L2, ^{233}Pa in IC5, ^{231}Pa in IC3 (8.2 s), and in the second step, the half-mass intensity was analyzed in IC5, IC4, and IC3 (1.2 s, Fig. 3). Machine background was monitored between every sample and standard and relative to signal size of the GEOTRACES standard (see below) was about 0.5‰

for ^{230}Th, 0.03‰ for ^{232}Th, and 2‰ for ^{231}Pa.

The short half-life of ^{233}Pa (26.975 d; Usman and Macmahon 2000) means that its continued decay leads to higher dark noise on whichever detector is used for analysis. At the outset, we experimented with allowing all ^{233}Pa to decay away to ^{233}U so that the analysis would not put ^{233}Pa onto any detector. However this method was discontinued because (a) the six-month wait time was too long, and (b) it was difficult to account for potential differences in ionization efficiency between uranium and protactinium. For these reasons, all ^{233}Pa analyses were made the day after column chemistry to ensure that all 233 was protactinium, and were made on a dedicated detector (IC5). During a full run the dark noise was remeasured between every two samples.

There is no way to make a long-term mass spectrometry consistency standard for the ^{231}Pa /^{233}Pa ratio because ^{233}Pa continually decays away to ^{233}U. For this reason, the only check on the accuracy is to analyze a ^{231}Pa solution that has gone through the entire chemical procedure to separate ^{233}Pa from ^{233}U. Here, we used the GEOTRACES intercalibration SW STD 2010-1 standard prepared at LDEO which has similar amounts of ^{231}Pa, ^{230}Th, and ^{232}Th to 10 L deep water from the central North Atlantic Ocean in a 0.5 g aliquot (Anderson et al. 2012).

Assessment and discussion

Despite previously published results using methods similar to our initial starting point (e.g., Chase et al. 2003), we found serious problems that we were able to solve during the course of the method development described above. In summary, the two major problems were both brought about by changes in the products procured from Bio-Rad, and as such, were not areas in which improvement was expected to be required. During the course of identifying these two problems, we were able to modify and streamline the process to provide a method for routine analysis of Th and Pa in seawater.

To determine how well the method worked we performed repeat analyses on the GEOTRACES SW STD 2010-1 standard over 18 months (*n* = 27). All of these analyses were performed by adding ~0.5 g of the standard to a precleaned 10 L (5 L) cubitainer (using an equivalent size to the samples being measured) containing ~8 L (5 L) of Milli-Q® water to provide the closest analogue possible to real seawater samples. At first, the uncertainties were dominated by the procedural blank, giving final uncertainties on concentration of up to 3% for ^{230}Th and 5% for ^{232}Th. These uncertainties were calculated to include the contributions from (a) blank using the variance of the blanks measured with the standards, (b) standard error of the ratios of the 40 cycles of the analysis (typically close to counting statistics), and (c) spike calibration. As the procedural blank was reduced, the uncertainties from the blank correction were reduced, giving more precise concentration measurements (Fig. 5). However the external reproducibility was greater than the precision calculated, with a reproducibility of
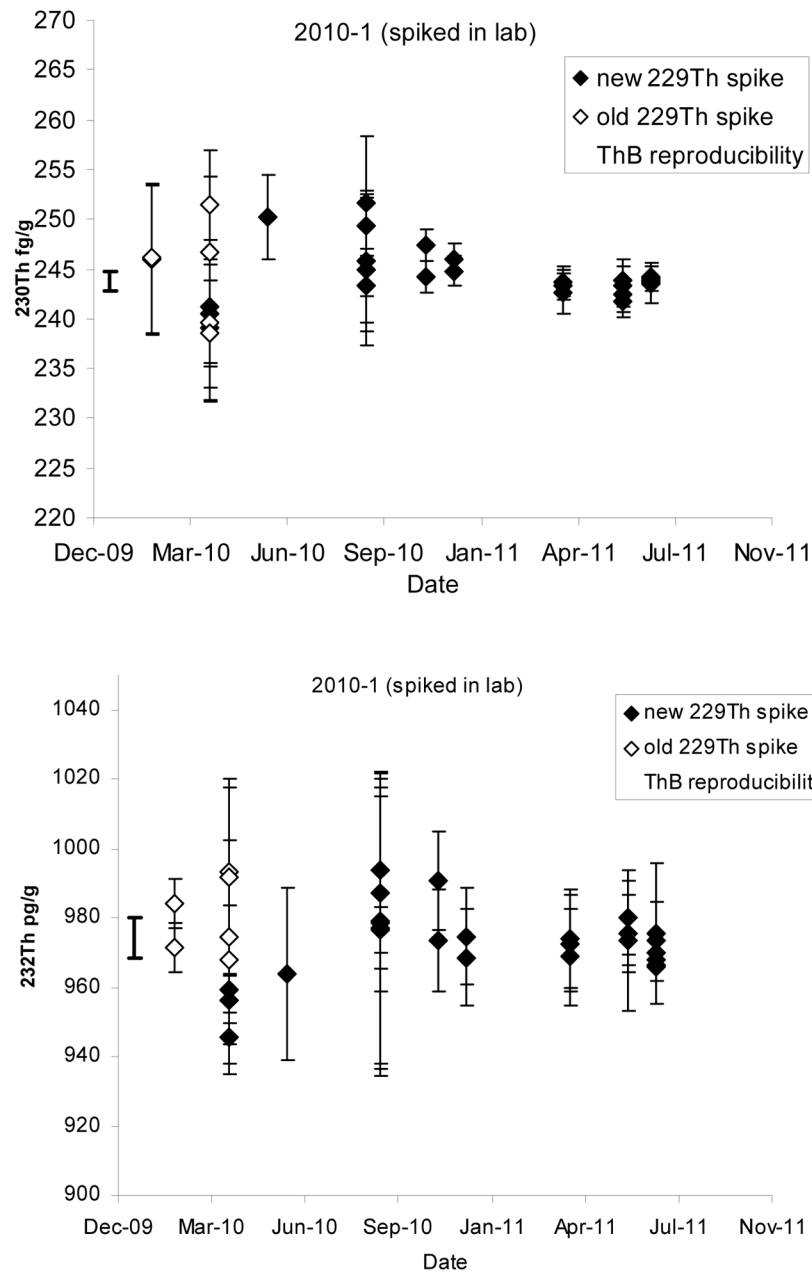
Fig. 5. Reproducibility of GEOTRACES SW standard 2010-1 from February 2010 to July 2011 (for information on standard see Anderson et al. 2012). Error bars on individual points include uncertainty from (a) blank correction, (b) standard error of repeat cycles during analysis, (c) spike calibration. The reproducibility of the in-house ThB mass spectrometry standard, as a percentage around the mean of the 2010-2011 analyses (error bars with no symbol, located to the left of the data; calculated from ^{230}Th/^{229}Th on top panel and ^{232}Th/^{229}Th on bottom panel) is shown to provide an assessment of the analytical reproducibility.

2.5% for ^{230}Th and 1.8% for ^{232}Th (2 SD, $n = 18$). Given that the range of values in a typical Atlantic water column profile spans an order of magnitude, this level of reproducibility is sufficient for the GEOTRACES analyses.

Our ^{231}Pa chemical procedure and analyses also improved in line with the Th analyses, with increases to the yield and the decreases in the background contamination. Repeat analyses of

the GEOTRACES SW STD 2010-1 standard gave a reproducibility of 4% with three different ^{233}Pa spikes ($n = 15$ over 14 months).

The procedure for pre-concentrating the seawater samples is straightforward but time consuming. For example, it takes ~40 (25) min to suck each 10 L (5 L) sample down to a volume of less than 500 mL. With our current method a batch of 16 samples (including blanks and standards) takes 10 d to

process, although the time between steps means that two sets of samples can be staggered and processed in overlapping time periods. A day is required for each set of Th analyses and each set of Pa analyses by MC-ICP-MS.

Comments and recommendations

In this article, we have shown improvements to the chemical procedure for purifying Th and Pa in seawater. The method developments outlined in this article illustrate the need to constantly monitor the reagents and consumables used in contaminant-prone analyses. We also document the analysis of Th and Pa by MC-ICP-MS. Our final procedure gives a reproducibility of 2.5% for ^{230}Th, 1.8% for ^{232}Th, and 4% for ^{231}Pa over approximately a 1-y period. Overall, we found that analysis of the GEOTRACES SW STD 2010-1 standard was a key to improving the method, and would recommend that this standard be analyzed with each batch of GEOTRACES samples. Although these improvements were made specifically for analysis of GEOTRACES samples, the lessons learned during this intercalibration process will be of value to those analyzing U-Th-Pa (and rare earth elements) as part of the GEOTRACES program. We anticipate that these improvements will also aid those using U-series isotopes in other applications that require high yields and low blanks, such as geochronology or weathering studies.

References

Anderson, R., M. Q. Fleisher, L.F. Robinson, R.L. Edwards, J. Hoff, M. Rutgers van der Loeff, and A. Thomas. 2012. GEOTRACES Intercalibration of ^{230}Th, ^{232}Th, ^{231}Pa and ^{10}Be. Limnol. Oceanogr. Methods 10:179-213 [doi:10.4319/lom.2012.10.179].

Anderson, R. F., and A. P. Fleer. 1982. Determination of natural actinides and plutonium in marine particulate material. Anal. Chem. 54:1142-1147 [doi:10.1021/ac00244a030].

Bacon, M., and R. Anderson. 1982. Distribution of thorium isotopes between dissolved and particulate forms in the deep sea. J. Geophys. Res. 87:2045-2056 [doi:10.1029/JC087iC03p02045].

Burke, A., and L. F. Robinson. 2012. The Southern Ocean's role in carbon exchange during the last deglaciation. Science [doi:10.1126/science.1208163].

Chase, Z., R. F. Anderson, M. Q. Fleisher, and P. W. Kubik. 2003. Scavenging of Th-230, Pa-231, and Be-10 in the Southern Ocean (SW Pacific sector): the importance of particle flux, particle composition and advection. Deep-Sea Res. II 50:739-768 [doi:10.1016/S0967-0645(02)00593-3].

Chen, J. H., R. L. Edwards, and G. J. Wasserburg. 1986. U-238, U-234 and Th-232 in seawater. Earth Planet. Sci. Lett. 80:241-251 [doi:10.1016/0012-821X(86)90108-1].

Choi, M. S., and others. 2001. Rapid determination of ^{230}Th and ^{231}Pa in seawater by desolvated micro-nebulization inductively coupled plasma mass spectrometry. Mar. Chem. 76:99-112 [doi:10.1016/S0304-4203(01)00050-0].

Geotraces Planning Group. 2006. GEOTRACES Science Plan. Scientific Committee on Oceanic Research.

Moran, S. B., M. A. Charette, J. A. Hoff, R. L. Edwards, and W. M. Landing. 1997. Distribution of ^{230}Th in the Labrador Sea and its relation to ventilation. Earth Planet. Sci. Lett. 150:151-160 [doi:10.1016/S0012-821X(97)00081-2].

———, C. -C. Shen, H. N. Edmonds, S. E. Weinstein, J. N. Smith, and R. L. Edwards. 2002. Dissolved and particulate ^{231}Pa and ^{230}Th in the Atlantic Ocean: constraints on intermediate/deep water age, boundary scavenging, and ^{231}Pa/^{230}Th fractionation. Earth Planet. Sci. Lett. 203:999-1014 [doi:10.1016/S0012-821X(02)00928-7].

Nozaki, Y., and M. Yamada. 1987. Thorium and protactinium isotope distributions in waters of the Japan Sea. Deep Sea Res. A 34:1417-1430 [doi:10.1016/0198-0149(87)90135-X].

Robinson, L. F., N. S. Belshaw, and G. M. Henderson. 2004. U and Th concentrations and isotope ratios in modern carbonates and waters from the Bahamas. Geochim. Cosmochim. Acta 68:1777-1789 [doi:10.1016/j.gca.2003.10.005].

———, J. F. Adkins, L. D. Keigwin, J. Southon, D. P. Fernandez, S. L. Wang, and D. S. Scheirer. 2005. Radiocarbon variability in the Western North Atlantic during the last deglaciation. Science 310:1469-1473 [doi:10.1126/science.1114832].

Thomas, A. L., G. M. Henderson, and L. F. Robinson. 2006. Interpretation of the 231Pa/230Th paleocirculation proxy: New water-column measurements from the southwest Indian Ocean. Earth Planet. Sci. Lett. 241:493-504 [doi:10.1016/j.epsl.2005.11.031].

Usman, K., and T. D. Macmahon. 2000. Determination of the half-life of 233Pa. Applied Radiat. Isot. 52:585-589 [doi:10.1016/S0969-8043(99)00214-6].