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A new method to extract ^{232}Th, ^{230}Th and ^{231}Pa from seawater using a bulk-extraction technique with Nobias PA-1 chelating resin

Paulina Pinedo-González [a,*], Robert F. Anderson [a,b], Sebastián M. Vivancos [a,b], Frank J. Pavia [a,b,c], Martin Q. Fleisher [a]

[a] Lamont-Doherty Earth Observatory of Columbia University, Palisades, NY, USA
[b] Department of Earth and Environmental Sciences, Columbia University, New York, NY, USA
[c] Department of Geological and Planetary Sciences, California Institute of Technology, Pasadena, CA, USA

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ABSTRACT

The long-lived radioisotopes of Th and Pa are unique tracers for quantifying rates of biogeochemical processes in the ocean. However, their generally low concentrations (sub-fg/kg for ^{230}Th and ^{231}Pa and pg/kg for ^{232}Th) in seawater make them difficult to measure. Here, we present a new approach to determine ^{232}Th and ^{230}Th using Nobias PA-1 chelating resin following a bulk-extraction technique, and report for the first time the use of this resin to measure ^{231}Pa concentrations. This method has high extraction efficiency (>80%) at pH of 4.4 ± 0.2 and the lowest procedural blanks reported in the literature: 1.0 ± 0.2 pg, 0.10 ± 0.03 fg, and 0.02 ± 0.01 fg for ^{232}Th, ^{230}Th, and ^{231}Pa, respectively, representing 3%, 0.02%, and 0.01% of the total dissolved ^{232}Th, ^{230}Th, and ^{231}Pa found in 5 L of a typical low-concentration surface seawater sample from the subtropical Pacific Ocean. The procedure yields data with high precision for all three isotopes (0.76% for ^{232}Th, 0.89% for ^{230}Th, and 0.96% for ^{231}Pa, 2σ), allowing us to reliably measure Th and Pa in the oceans even at concentrations as low as those found in surface waters of the South Pacific Ocean. The accuracy of this method was confirmed by the analysis of well-characterized standard solutions (SW STD 2010-1 and SW STD 2015-1) and seawater samples collected aboard the *FS Sonne* (cruise SO245) during the UltraPac cruise in the South Pacific Ocean. Simultaneous and rapid extraction of ^{232}Th, ^{230}Th and ^{231}Pa from seawater, as well as the high precision and accuracy of this method makes it ideal for both spatially and temporally high-resolution studies.

1. Introduction

The ocean plays a major role in regulating Earth's climate through the storage and transport of heat, nutrients and carbon. In order to study these features, multiple geochemical and isotopic tracers have been developed to evaluate modern and past changes in oceanic processes that regulate them (e.g., nutrient cycling and supply [1]), redox conditions [2]), ocean circulation patterns [3]). The long-lived radioisotopes of thorium (Th) and protactinium (Pa) have been recognized as excellent tracers for a wide range of oceanographic processes, including particle cycling and carbon export flux [4,5]) and quantifying lithogenic fluxes of trace elements to the marine environment [6–8]).

Th and Pa isotopes provide information about biogeochemical cycles in the ocean because of their well-constrained sources [9]. The radiogenic isotopes ^{230}Th ($t_{1/2}$ = 75,690 years) [10] and ^{231}Pa ($t_{1/2}$ = 32,760 years) [11] are produced at a uniform rate throughout the water column by the radioactive decay of ^{234}U and ^{235}U, respectively. ^{232}Th ($t_{1/2} = 1.4 \times 10^{10}$ years) is primordial and enters the ocean via the dissolution of lithogenic matter. Thorium and protactinium are extremely reactive towards particles and are rapidly removed from the water column by adsorption onto particulate matter. Because the scavenging residence times for ^{231}Pa (50–200 years) and ^{230}Th (10–40 years) are much shorter than their respective half-lives, their removal from the water column can be treated as being quantitatively equal to their known production rates, an assumption that is backed by modeling efforts [12,13] and sediment trap studies [14]. This property has been employed to study particle scavenging rates in a number of different oceanic environments [4,7]. Another application of the long-lived thorium isotopes (^{232}Th and ^{230}Th) is the study of modern dust inputs to the ocean and residence times of dissolved trace metals in the water column [6,8,15,16]. Application of the 1-D budget for ^{230}Th between radiogenic production and scavenging removal to ^{232}Th allows for the determination of ^{232}Th input rates, and

* Corresponding author.
E-mail address: papinedo@ldeo.columbia.edu (P. Pinedo-González).

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thus lithogenic material input rates [6,17,18].

Due to the particle reactive character of both Th and Pa, their dissolved concentrations in seawater are in the sub-fg/kg (^{230}Th and ^{231}Pa) or pg/kg (^{232}Th) levels. These extremely low concentrations represent the most significant challenge associated with their analysis. Studies have therefore used methods to separate and purify Th and Pa from the sea-salt matrix before analysis by mass spectrometry. Previous approaches include co-precipitation with $Fe(OH)_3$ and resin ion-exchange chromatography [19–21], or adsorption on MnO_2 coated filters and anion-cation exchange followed by solvent extraction [22]. These procedures are time consuming, taking up to 7 days for the preconcentration step. In addition, they require the purification of the co-precipitation or adsorbing agent, the use of concentrated HF to digest silicates, and a fair amount of sample handling, providing several opportunities for contamination or loss of the analytes of interest.

Chelating resins have provided an efficient tool for the preconcentration of a variety of trace metals and REE from seawater [23–26]. The commercially available Nobias Chelate PA1 resin has been applied for the separation and preconcentration of Th from seawater samples [25, 27–29]. However, the preconcentration of ^{231}Pa with this or any other chelating resin has never been reported in the literature.

^{230}Th and ^{231}Pa are often studied together [9] because the ^{231}Pa/^{230}Th ratio provides information about scavenging processes and about ocean circulation. To better support the common measurement of these isotopes, this work presents a new method to simultaneously extract ^{232}Th, ^{230}Th and ^{231}Pa from seawater by bulk extraction onto Nobias PA-1 chelating resin, followed by purification by anion exchange chromatography and determination by ICP-MS.

2. Materials and methods

2.1. Materials and chemicals

All chemicals used in this study were ultrapure grade. Concentrated HCl and HNO_3 were produced by distillation of trace metal grade acids in a DST-1000 Acid Purification System (Savillex). H_2O_2, CH_3COOH, and NH_4OH were Optima Grade (Fisher Chemical) and used as received. All water was >18.2 MΩ from a Milli-Q purification system (Millipore Corp.). Ammonium acetate buffer solution was prepared by mixing NH_4OH (25%, 13 M), acetic acid glacial (17.4 M) and Milli-Q water in a 1.3:1:1 (v:v:v) ratio, and then adjusted to pH 6.2 ± 0.2 with NH_4OH and acetic acid. All pH adjustments were carried out with a pH meter (Thermo Scientific). Resin is cleaned, separated from the seawater, and eluted using a PFA filtration apparatus that consists of a 4-inch PFA filter inlet cup attached to a 47 mm filter holder (Savillex) with 3 μm polycarbonate membranes (Whatman Nuclepore). The filter holder's outlet as well as the receiving container sits inside an acrylic tube connected to a vacuum pump (Fig. 1S). All polyethylene labware material 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. Teflon beakers (Savillex) and filter holder (Savillex) were cleaned by immersion in 1% Citrad detergent followed by 3 days in a hot (~90 °C) 8 M HNO_3 bath and extensive rinsing with Milli-Q water. New Nobias PA-1 chelating resin was obtained from Hitachi High Technologies, Japan and cleaned by leaching in 4 changes of 3 M HNO_3 over two weeks. Cleaned resin was then pre-measured and stored in 15 mL vials each containing ~2.5 mL aliquots of resin in 3M HNO_3. Isotope yield monitor solutions, ^{229}Th and ^{233}Pa, were used for isotopic dilution analysis and elemental yield control.

2.2. Th and Pa extraction from seawater

Th and Pa were extracted from seawater using a bulk-extraction technique with Nobias PA-1 chelating resin. This resin has successfully been used to extract Th from seawater before analysis by ICP-MS [25, 27–29]. These methods, however, employ complex equipment; packed columns or cartridges, manifolds, pumps and tubing, providing multiple opportunities for sample contamination and loss. Instead, we opted to use a bulk-extraction technique. This technique is faster and cleaner because the extraction is performed in the original sample container.

The full protocol for the preconcentration of Th and Pa from seawater is shown in Fig. 1; 5 L of seawater samples acidified at sea to pH of 1.7 are spiked with weighed amounts of isotope yield monitors (about 1 pg of ^{229}Th and 0.1 pg of ^{233}Pa for each sample). After spike equilibration (≥8 h), sample pH is raised by addition of 1 mL (per L of seawater) of ammonium acetate buffer and then adjusted to 4.4 ± 0.2 with HCl and NH_4OH. Although the amount of NH_4OH is sample dependent, an average of 8 mL is needed to raise 5 L of seawater from a pH of 1.7–4.4. To avoid wasting too much sample adjusting the pH, the pH of the sample is first monitored pipetting ~50 μL onto a pH strip (range 4.0–7.0). Once the sample is around 4.4, the pH is fine-adjusted with a pH meter by pouring a small aliquot (~5 mL) from the sample into a secondary container. After pH adjustment, 2.5 mL (~0.63 g) of clean Nobias resin is added to each sample. The capacity of the resin has been determined to be 0.16 ± 0.01 mmol/g using Cu^{2+} [25], thus the 2.5 mL of resin employed here is sufficient to collect the target ions (Th and Pa) quantitatively from 5 L of seawater even if other trace metals are also being adsorbed at the same pH. Resin is re-suspended in the vial containing the pre-measured clean resin and poured into the filtration apparatus. It is then rinsed with 100 mL of Milli-Q water and decanted

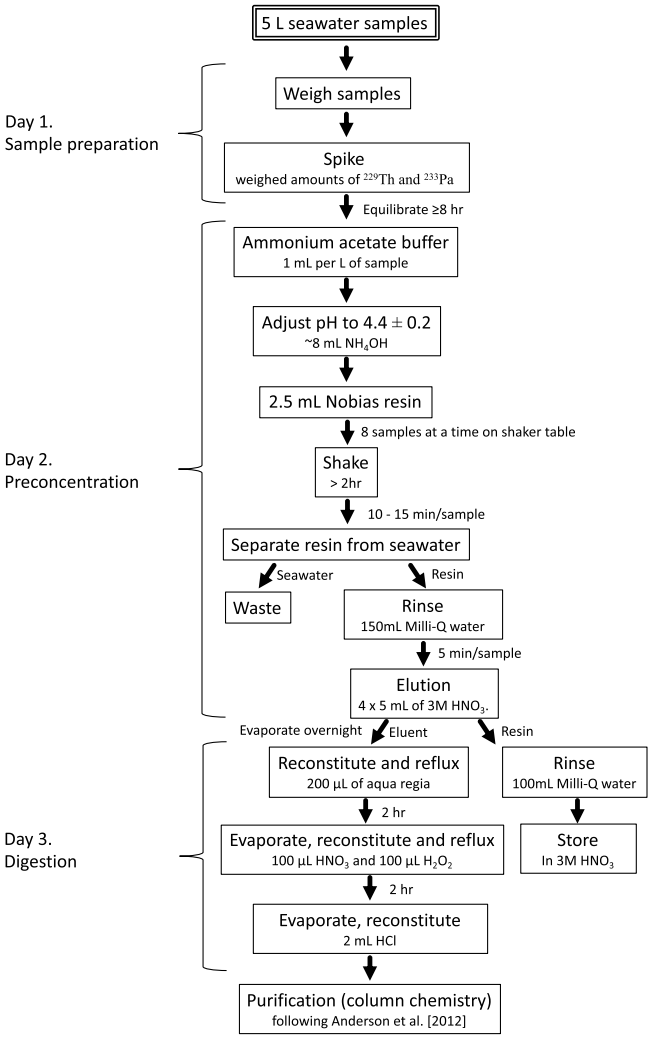

Fig. 1. Brief procedural outline for extraction of ^{232}Th, ^{230}Th and ^{231}Pa from seawater with Nobias PA-1 chelating resin.

into the seawater sample by pouring some of the sample into the filtration rig to resuspend the resin. Sample is then vigorously shaken on a shaker table for at least 2 h. The shaker table used in our laboratory is equipped to shake 8, 5-L cubitainers at a time. After shaking, resin is separated from the seawater by filtration using the filtration apparatus (Fig. 1S). The resin is then rinsed with 100 mL Milli-Q water to remove salts. Th and Pa are eluted from the resin in the same filter holder with 4 × 5 mL of 3 M HNO_3 and collected in a 30 mL Teflon vial. After metal collection, sample solutions are evaporated and treated with a mixture of H_2O_2, HCl, and HNO_3 to destroy organics. The resin in the filter is then rinsed with 100 mL of Milli-Q water and washed out of the filtration rig with 3 M HNO_3 into a 15 mL vial for storage. Storing and reusing the resin offers several advantages over previous extraction techniques (i.e., co-precipitation with $Fe(OH)_3$ or adsorption on MnO_2 coated filters). Metals are quantitatively eluted from the resin, making it possible to reuse it directly from the storage vial without any further cleaning, which saves time, generates less waste and avoids the hassle of purifying the co-precipitation or adsorption agents.

2.3. Sample purification

Following extraction, Th and Pa were purified by ion exchange chromatography using a series of three columns packed with Bio-Rad AG1-X8 100–200 mesh anion resin following the procedure described in Anderson et al. [19]. Briefly, new Bio-Rad AG1-X8 resin is cleaned by leaching in 6 M HCl followed by 0.12 M HCl/0.29 M HF and rinsed with Milli-Q water. This is repeated 5 times. After cleaning, disposable chromatography polyethylene columns of 2.5 mL total volume and with a porous frit of 30 μm pore size (Environmental Express) are packed with 1 mL of clean resin. All columns are then cleaned and conditioned with 3 mL concentrated HCl/0.14 M HF followed by 2 × 2 mL concentrated HCl. After the conditioning step, the samples are loaded onto the column in concentrated HCl. The Th fraction is collected with 3 × 2 mL of concentrated HCl, while the Pa fraction is subsequently eluted with 3 × 2 mL of concentrated HCl/0.14 M HF. After the separation column, Pa is purified by loading onto the column (previously conditioned with 2 × 2 mL of concentrated HCl) in 1 mL of concentrated HCl, rinsing with 5 × 1 mL of concentrated HCl and eluting Pa with 3 × 2 mL of concentrated HCl/0.14 M HF. The Th fraction is purified by loading the sample onto the column (conditioned with 2 × 2 mL 8 M HNO_3) in 1 mL of 8 M HNO_3, rinsing with 5 × 1 mL of 8 M HNO_3 and eluting Th with 3 × 2 mL of concentrated HCl. Although it is beyond the scope of this work, it is worthwhile to mention that the 8 M HNO_3 fraction contains the rare earth elements, opening the possibility to measure REE concentrations or Nd isotopes from the same seawater sample (see also Section 3.1). After column chemistry, samples for both Th and Pa isotopes are evaporated and reconstituted in 500 μL of 0.16 M HNO_3/0.028 M HF, which yields a pre-concentration factor of about 10,000.

2.4. Instrumentation

Concentrations of ^{230}Th, ^{232}Th, and ^{231}Pa were determined by isotope dilution, with measurements made on a Thermo ELEMENT XR Single Collector Magnetic Sector ICP-MS, equipped with a Jet interface pump. Optimized instrument conditions are listed in Table 1. Solutions were introduced to the ICP-MS using a Cetac™ Aridus I desolvating nebulizer to improve sensitivity and decrease oxide/hydride formation. Enhanced sensitivity Jet sample and X-skimmer cones were used for all measurements. Th and Pa isotopes were analyzed in separate runs. The isotopes measured were ^{229}Th and ^{230}Th (counting mode), and ^{232}Th (in analog mode) for Th analyses, and ^{231}Pa, ^{232}Th, and ^{233}Pa (in counting mode) for Pa analyses. To monitor mass bias/amu and analog/counting correction factors, ^{234}U, ^{235}U, ^{238}U were also measured in a natural U standard in both counting and analog modes.

We used a 30 ppt solution of natural U (SRM129) as the isotopic standard for measuring the mass bias effects during isotope ratio mass spectrometry (assuming that the mass fractionation for Th and Pa are the same as for U). We used the internal normalization technique, in which we employ a known isotope ratio (^{238}U/^{235}U) to determine mass bias during the run and to correct the isotope ratio of interest. When we are making Th measurements, we make a second set of measurements of the SRM129 standard at a higher concentration (2 ppb) to determine the instrumental analog/counting calibration factor, after correcting for mass bias effects.

To correct for the instrument background count rates, we bracketed each sample measurement with an acid blank (1% HNO_3/0.1% HF). A series of ^{232}Th standards were run to correct tailing of ^{232}Th onto masses 231 and 233 for Pa analyses, and masses 230 and 229 for Th analyses. For each Th run, we run a set of external ^{232}Th standards covering the concentration range of ^{232}Th in samples. For Pa analyses, the ^{232}Th in the Pa fraction is less than 2 pg/g, so a different set of low concentration ^{232}Th standards is used. A linear regression of counts on mass 232 against the mass of interest (229, 230, 231, or 233) is used to get tailing equations for each mass. The slope of the regression is an estimate of the abundance sensitivity at each mass (typically 1–3 ppm for ^{230} Th at 2 amu). Often, the ^{232}Th signal is so small in the Pa fractions that no tailing correction is needed. Concentrations of ^{230}Th, ^{232}Th and ^{231}Pa were determined by isotope dilution [30], using ^{229}Th (~1 pg/sample) and ^{233}Pa (~0.1 pg/sample) as spikes.

Table 1
Optimized instrument and data acquisition parameters.

Instrument settings	
Instrument	ELEMENT XR Single Collector Magnetic Sector
Sample cone	Nickel, Jet-cone
Skimmer cone	Nickel, X-cone
Cooling gas	16 liters/min
Auxiliary gas	0.6–0.75 liters/min
Sample gas	0.6–0.8 liters/min
Data acquisition	
Low resolution	m/Δm = 300
Monitored isotopes in counting mode	^{229}Th,^{230}Th,^{232}Th,^{231}Pa,^{233}Pa
Monitored isotopes in analog mode	^{232}Th
Scans	200
Points/peak width	100
Mass window (%)	5
Sub-sampling time	10–300 ms depending on the isotope
Total time of analysis	<3 min
Aridus I system	
Sample uptake rate	95 μl/min
N_2 gas	5–20 ml/min
Ar gas	3–4 liters/min
Temperature	spray chamber = 110 °C, membrane = 160 °C

3. Results and discussion

3.1. Effect of pH on Th and Pa extraction

Previous studies have shown that sample pH has an important effect on elemental yields when using the Nobias resin [23,24,27,28]. To evaluate this effect on the adsorption of Th and Pa onto the resin we carried out a series of experiments at different pH values. For this exploratory step we used 500 mL Milli-Q water samples spiked with ^{229}Th and ^{233}Pa. Samples were adjusted using 500 μL of buffer solution, NH_4OH and HCl to yield a sample pH range of 2.0–8.0. After pH adjustment, 2.5 mL of Nobias chelating resin was added to each sample and vigorously shaken for 2 h on a shaker table.

The recovery of ^{229}Th and ^{233}Pa from Nobias resin as a function of pH is shown in Fig. 2a. We found that Th was quantitatively collected (>90%) at pH values between 3 and 5, whereas for Pa, maximum yields (>90%) were found between 4 and 5.5. Thus, we determined the

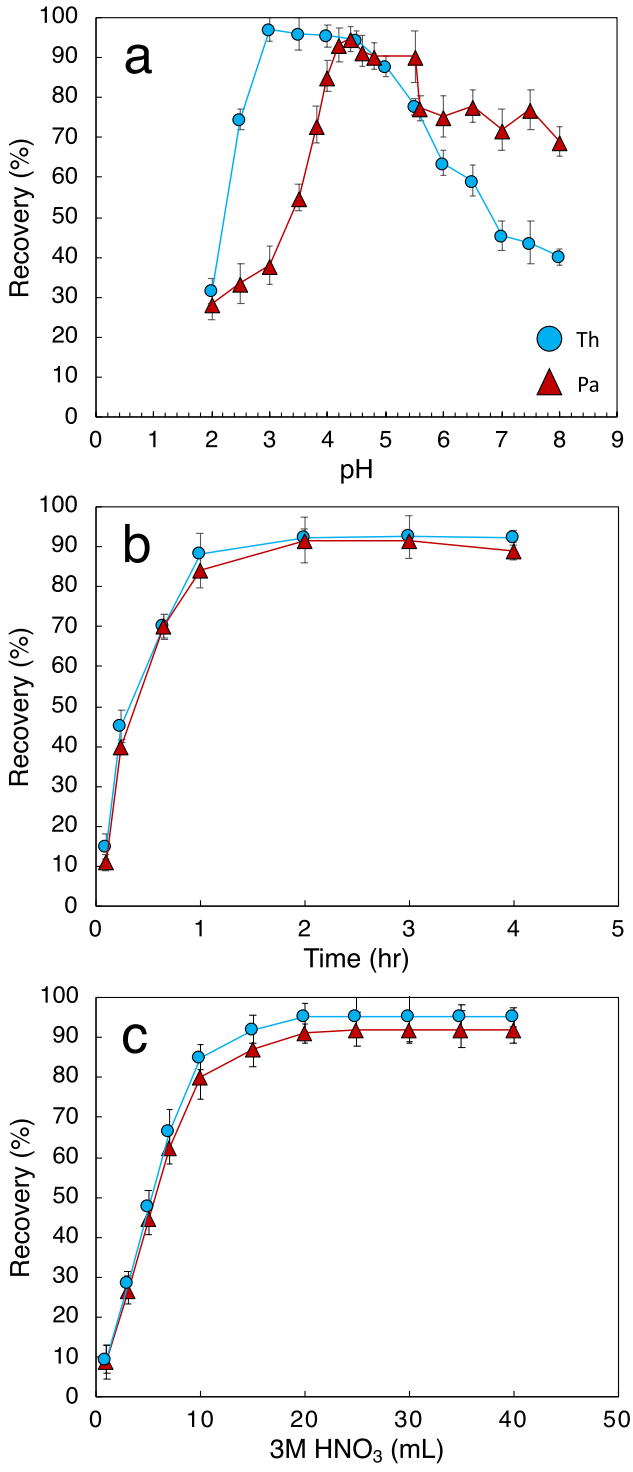

Fig. 2. Recoveries of ^{229}Th (circles) and ^{233}Pa (triangles) as a function of a, pH; b, shaking time; and c, elution volume with 3 M HNO_3. Error bars indicate the standard deviation of 3 replicate samples.

optimum sample pH for the simultaneous extraction of both Th and Pa to be at 4.4 ± 0.2. Similar data on recovery percentage versus pH have been reported for Th in previous studies [27,28]. Our results are generally consistent with these previous studies, except for the result reported by Takata et al. [28], which found that the optimum sample pH was between 2 and 3.

In addition, for those interested in the simultaneous pre-concentration of dissolved Th, Pa and Nd isotopes from a single seawater sample, it is worthwhile to mention that the rare earth elements (REEs) fraction is also extracted at a similar pH. Fig. 2S shows that Nd is quantitatively collected (>90%) at pH values above 3.5. This result is similar to the optimal pH for the extraction of Nd from seawater reported by Pérez-Tribouillier et al. [27].

3.2. Optimum shaking time

Because we use a bulk-extraction technique, shaking the sample is essential to achieve high elemental yields. Shaking greatly increases the resin's surface area in contact with the seawater sample, allowing for equilibrium to be established more rapidly. To study the effect of shaking time on the adsorption of Th and Pa onto the resin, we spiked a series of 500 mL Milli-Q samples, adjusted them to pH 4.4 ± 0.2, and shook them for different periods of time on a shaker table. Fig. 2b shows the recovery of ^{229}Th and ^{233}Pa from Nobias resin as a function of shaking time. We found that when the samples are shaken vigorously enough to keep the resin suspended in the seawater, there are no significant differences in the recovery of Th and Pa beyond 2 h.

3.3. Volume of elution

After the extraction step, resin is separated from the seawater by filtration in a PFA filter apparatus with a 47 mm filter holder and a 3 μm polycarbonate membrane. Th and Pa is then eluted from the resin in the same filter holder with 3 M HNO_3. To evaluate the elution efficiency of Th and Pa, we tested different elution volumes following extraction onto resin from a series of 500 mL Milli-Q samples spiked with ^{229}Th and ^{233}Pa. These results are plotted in Fig. 2c. We found that 2 × 5 mL aliquots of 3 M HNO_3 are enough to elute most of the sample (>85%) from the resin. Yet, maximum recoveries are achieved with 15–20 mL of 3 M HNO_3. Thus, to ensure complete elution of Th and Pa from the resin we used 4 × 5 mL of 3 M HNO_3 in this study.

3.4. Procedural blanks and sample size

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 < 0.027 pg of ^{232}Th for a 5 L sample, based on published specifications from the manufacturer.

Procedural blanks for purification (column blanks) were estimated by loading five columns with 2 mL of concentrated HCl and processing them as samples. Mean and 1σ column blanks were ^{232}Th = 0.7 ± 0.1 pg, ^{230}Th = 0.05 ± 0.01 fg, and ^{231}Pa = 0.009 ± 0.002 fg. Total procedural blanks were determined by adding 4.5 L of Milli-Q water to 6 acid-cleaned 5-L cubitainers, acidifying to pH = 2, spiking with ^{229}Th and ^{233}Pa, and then treating them as samples. Mean and 1σ procedural blanks were ^{232}Th = 1.0 ± 0.2 pg, ^{230}Th = 0.10 ± 0.03 fg, and ^{231}Pa = 0.02 ± 0.01 fg. For comparison, 5 L of surface seawater from the North Pacific gyre (station ALOHA) contains 30 pg of ^{232}Th (~6 pg/kg), 550 fg of ^{230}Th (~110 fg/kg), and 205 fg of ^{231}Pa (~41 fg/kg), hence our total procedural blanks represent 3%, 0.02%, and 0.01% of the total dissolved ^{232}Th, ^{230}Th, and ^{231}Pa, respectively, found in a 5-L sample of typical low-concentration surface seawater.

Procedural blanks for ^{232}Th, ^{230}Th, and ^{231}Pa are lower than any previously published method (Table 2). In our method, the column blank accounts for about 70%, 50%, and 45% of the total procedural blank for ^{232}Th, ^{230}Th, and ^{231}Pa, respectively. For comparison, in the iron coprecipitation method, the column blank constitutes only a small fraction of the total procedural blank (7%, 13%, and 14% for ^{232}Th, ^{230}Th, and ^{231}Pa), indicating that using Nobias resin results in a cleaner extraction. These results also indicate that future efforts towards obtaining even lower procedural blanks should be directed at improving the purification step (column chemistry). Simple modifications like reducing the column size (and thus the amount of resin and reagents)

Table 2
Comparison of purification blank, total procedural blank, recovery, LOD, sample volume, and preconcentration factor obtained with different pre-concentration techniques for ^{232}Th, ^{230}Th, and ^{231}Pa analysis in seawater.

Separation method	Purification blank					Total procedural blank					Recovery	LOD	Sample volume (L)	Pre-concentration factor	Reference
	^{232}Th (pg)	s. d.	^{230}Th (fg)	s.d.	^{231}Pa (fg)	s.d.	^{232}Th (pg)	s. d.	^{230}Th (fg)	s.d.	^{231}Pa (fg)	s.d.				
Bulk extraction w/ Nobias resin	0.7	0.1	0.05	0.01	0.009	0.002	1.0	0.2	0.10	0.03	0.02	0.01	>80%	0.6 pg for ^{232}Th 0.09 fg for ^{230}Th 0.03 fg for 231Pa	5	10,000	This study
Fe coprecipitation	0.7	0.1	0.08	0.01	0.010	0.002	9.0	0.9	0.6	0.2	0.07	0.02	>70%	2.7 pg for ^{232}Th 0.6 fg for ^{230}Th 0.06 fg for ^{231}Pa	5	10,000	[19]
Fe coprecipitation	–	–	1.0	0.4	0.20	0.09	–	–	3.8	0.9	0.43	0.16	>50%	0.15 fg/kg for ^{230}Th 0.02 fg/kg for ^{231}Pa	10–20	>33,000	[21]
Adsorption by Nobias resin	–	–	–	–	–	–	3.8 (per kg)	–	–	–	–	–	>90%	3.8 pg/kg for ^{232}Th	0.2	40	[28]
Adsorption by Nobias resin	1.0	0.6	–	–	–	–	10.0	3.1	0.9	–	–	–	>90%	–	5–10	8000–16,000	[27]
SeaFAST w/Nobias column	–	–	–	–	–	–	5 pg (per kg)	–	–	–	–	–	>75%	5 pg/kg for ^{232}Th	0.02	50	[29]

LOD: Limit of detection. In this study, LOD is calculated as 3 * s.d. of the total procedural blank [24].
All studies used ICP-MS as the analytical technique.

could lower the blanks even further. Nonetheless, our total procedural blanks are lower than those reported by Takata et al. [28] and Pérez-Tribouillier et al. [27], which also utilize Nobias resin for the extraction step. This indicates that a bulk extraction procedure is an excellent alternative for samples that require low blank levels.

Of the isotopes targeted in this study, ^{232}Th poses the highest risk of contamination. For this reason, measurements of ^{232}Th typically require large sample volumes to minimize the contribution from procedural blanks. The low blanks attained from using this technique suggest that it can be reliably adapted to process smaller sample volumes, opening new avenues of research.

^{230}Th and ^{231}Pa are not as prone to contamination as ^{232}Th during sample purification and handling because their relative concentrations in crustal material compared to seawater are much lower than for ^{232}Th which has a concentration six orders of magnitude higher in crust than seawater. However, due to the extremely low concentrations of ^{230}Th and ^{231}Pa in surface seawater, the sample volume needed to accurately determine their concentrations is restricted by the limit of detection, hence the need for large volume samples. Nonetheless, low blanks greatly improve the accuracy and precision of the measurements.

3.5. Reproducibility and accuracy

The reproducibility and accuracy of an analytical method are by far the most important determinants of analytical method quality. These parameters were assessed by the analysis of two intercalibrated working standard solutions of ^{232}Th, ^{230}Th, and ^{231}Pa, SW STD 2010-1 [19] and SW STD 2015-1, and seawater samples from the South Pacific Ocean. First, 20 × 4.5 L of Milli-Q water were added to acid-cleaned 5-L cubitainers and spiked with the isotope yield monitors (about 1 pg of ^{229}Th and 0.1 pg ^{233}Pa for each sample), then a weighed 100 μL aliquot of either seawater standard 2010-1 (n = 10) or 2015-1 (n = 10), which has about 6 times lower ^{232}Th concentration, was added to the cubitainers to be processed as full water samples. Results are shown in Table 3; all values for the seawater standard 2010-1 are in agreement with recent consensus values. The reproducibility for each isotope at the 95% confidence level (2σ) was 0.76% for ^{232}Th, 0.89% for ^{230}Th, and 0.96% for ^{231}Pa on SW STD 2010-1, and 1.01% for ^{232}Th, 0.88% for ^{230}Th, and 1.26% for ^{231}Pa on SW STD 2015-1. The elemental yield for these samples was >90%.

To further test the reproducibility and accuracy of the developed analytical method, we analyzed 10 seawater samples collected on the UltraPac transect between Chile and New Zealand in the South Pacific Ocean (station 5, water depths: 10 m, 100 m; station 7, water depths: 20 m, 50 m; station 9, water depth: 20 m; station 13, water depths: 20 m, 50 m, 100 m, 200 m, 400 m). The selected 10-L samples were transferred to new 5-L acid-cleaned cubitainers and analyzed as independent samples. First, we compared results from our newly developed bulk-extraction method with those obtained by the iron coprecipitation method. To accomplish this, we generated a set of identical samples by splitting the original 10-L samples from station 5 [23.5°S, 106.9°W], 7 [25.9°S, 114.0°W], and 9 [30.6°S, 121.8°W] into two 5-L samples. We then analyzed each set of 5-L samples using a different method for each sample in the set. Levels of ^{232}Th, ^{230}Th, and ^{231}Pa obtained by the bulk-extraction technique as well as the Fe coprecipitation method are plotted in Fig. 3. In general, results of both methods matched within uncertainty for all samples, indicating that the developed analytical method is suitable for the determination of low levels of ^{232}Th, ^{230}Th, and ^{231}Pa in seawater samples.

To put our results in context and to demonstrate the quality of the data obtained by our developed analytical technique, we compare our duplicate measurements from station 13 [39.0°S, 150.0°W] with those of station 12 [39.3°S, 139.8°W] and 14 [39.0°S, 160.0°W] generated by the Fe coprecipitation method [31,32]. Fig. 4 shows that our results are within the range reported by Pavia et al. [31] and Anderson and Fleisher [32] for samples analyzed in 2017–2018. In addition, our results show

Table 3
^{232}Th, ^{230}Th, and ^{231}Pa concentrations in intercalibrated working standard solutions SW STD 2010-1 and SW STD 2015-1 obtained in this study and the reported consensus values. Reported errors represent 2-sigma measurement uncertainty.

		^{232}Th	2σ (%)	^{230}Th	2σ (%)	^{231}Pa	2σ (%)	
2010–1	n = 10	954.1 ± 7.2	0.76	246.0 ± 2.2	0.89	36.3 ± 0.3	0.96	This study
	n = 128	990.4 ± 48.2	4.87	248.0 ± 3.5	1.43	37.5 ± 2.6	7.13	Consensus
2015–1	n = 10	172.5 ± 1.7	1.01	205.9 ± 1.8	0.88	38.1 ± 0.5	1.26	This study
	n = 72	174.5 ± 14.0	8.04	206.4 ± 2.2	1.06	38.9 ± 1.2	3.22	Consensus

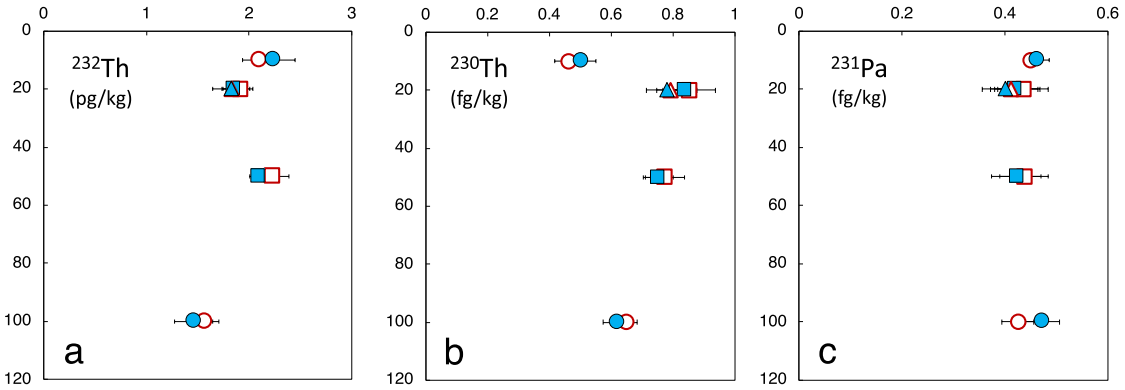

Fig. 3. Comparison between data obtained by the Fe coprecipitation method (empty symbols) and our analytical method that concentrates Th and Pa on Nobias resin (filled symbols). Water was collected during the UltraPac cruise (SO-245; *FS Sonne*. December 2015–January 2016) in the South Pacific Ocean. Samples were generated by splitting the original 10-L samples collected from station 5 (circles), 7 (squares), and 9 (triangles) into two 5-L subsamples and then analyzed using either $Fe(OH)_3$ co-precipitation or adsorption by Nobias resin. Error bars represent 1-sigma measurement uncertainty. Where not visible, error bars are smaller than the symbol size. Results of both methods matched within uncertainty for all samples.

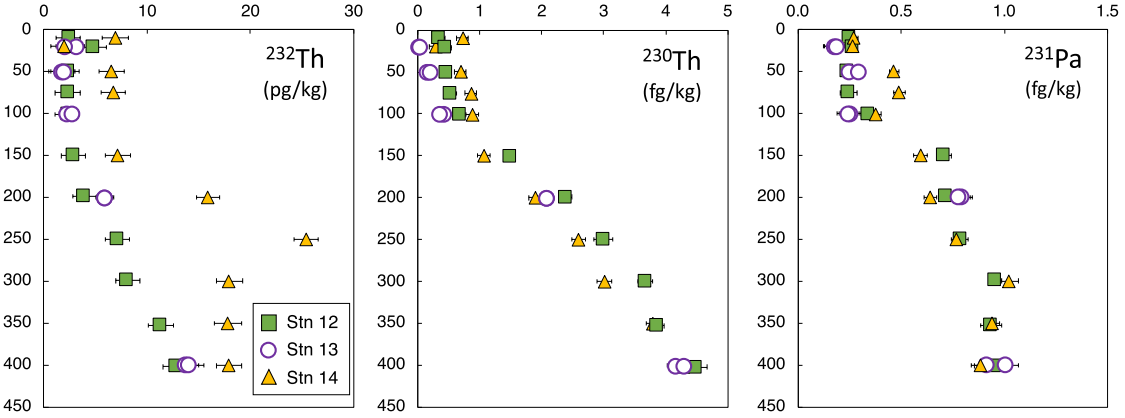

Fig. 4. Depth profiles from the UltraPac cruise in the South Pacific Ocean from station 12 [39.3°S, 139.8°W] (filled squares), station 13 [39.0°S, 150.0°W] (open circles), and station 14 [39.0°S, 160.0°W] (filled triangles). Data from station 12 and 14 were obtained by the Fe coprecipitation method and reported by Pavia et al. [31] (^{232}Th and ^{230}Th) and Anderson and Fleisher [32] (^{231}Pa). Data from station 13 were obtained by our analytical technique using Nobias resin. Duplicates were obtained by splitting the original 10-L samples into two 5-L subsamples and analyzing them separately. The elemental yield for these samples was >80%. Error bars represent 1-sigma measurement uncertainty. Where not visible, error bars are smaller than the symbol size.

excellent reproducibility for each isotope across all sample duplicates (less than 1% variation, nearly exact superimposition). These results demonstrate the ability of our analytical method to generate oceanographically consistent data for open ocean samples.

4. Conclusions

A new method to extract ^{232}Th, ^{230}Th and ^{231}Pa from seawater using a bulk-extraction technique with Nobias PA-1 chelating resin at pH 4.4 ± 0.2 has been presented. Low procedural blanks (^{232}Th = 1.0 ± 0.2 pg, ^{230}Th = 0.10 ± 0.03 fg, and ^{231}Pa = 0.02 ± 0.01 fg) and high extraction efficiency (>80%) allow the generation of precise and accurate measurements over almost the complete range of Th and Pa concentrations expected in the upper water column of the open ocean. Precision and accuracy have been evaluated by measuring aliquots of two standard solutions containing ^{232}Th, ^{230}Th, and ^{231}Pa and by analyzing seawater samples collected on the UltraPac cruise in the South Pacific Ocean. Measurements of the standard solutions were in agreement with recent consensus values and showed excellent reproducibility for each isotope (~1%). Data for samples from the UltraPac cruise were in agreement with measurements of the same sample extracted using the iron coprecipitation method as well as data reported in Pavia et al. [31] and Anderson and Fleisher [32] for samples collected a few degrees east (station 12) and west (station 14) during the same oceanographic

campaign.

This procedure allows for the precise and accurate combined analysis of ^{232}Th, ^{230}Th and ^{231}Pa in seawater using Nobias PA-1 chelating resin. Because it is quick and requires minimal sample preparation and handling, it is optimal for high-resolution sampling and large-scale projects that generate hundreds of samples (e.g., GEOTRACES). In addition, the low procedural blank obtained for ^{232}Th allows for its precise determination in samples with smaller sample volumes. This could create new avenues of research allowing for a more thorough investigation of the biogeochemical cycling of Th in the ocean.

CRediT authorship contribution statement

Paulina Pinedo-González: Conceptualization, Methodology, Investigation, Writing - original draft. **Robert F. Anderson:** Conceptualization, Funding acquisition. **Sebastián M. Vivancos:** Investigation, Writing - review & editing. **Frank J. Pavia:** Writing - review & editing. **Martin Q. Fleisher:** Resources.

Declaration of competing interest

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

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Appendix A. Supplementary data

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