J Radioanal Nucl Chem
DOI 10.1007/s10967-012-2047-9

Methodological advances for measuring low-level radium isotopes in seawater

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Received: 13 July 2012

Abstract A new approach for quantifying radium isotopes in seawater was developed in advance of the international GEOTRACES program, which has the goal of identifying processes and quantifying fluxes that control the distribution of trace elements and isotopes (TEIs) in the ocean. High-resolution water column samples were collected via a commercially available in situ pump modified to accept multiple filter media including a manganese-oxide (MnO_2) impregnated acrylic cartridge for extracting dissolved radionuclides from seawater. The modifications mitigated prefilter clogging and allowed for up to 1,800 L filtrations in 4 h of pumping. Different MnO_2 cartridge preparation methods were investigated to achieve maximum radium (Ra) extraction efficiency under high sample flow rates. Full-ocean depth profiles were measured for short-lived radium isotopes (^{223}Ra and ^{224}Ra) in shipboard laboratories using a delayed coincidence alpha scintillation counter (RaDeCC). Samples were reanalyzed 4 weeks and 2 months after collection for ^{228}Th and ^{227}Ac to correct for supported ^{224}Ra and ^{223}Ra, respectively. Finally, the cartridges were measured on a gamma-ray spectrometer for the long-lived radium isotopes (^{226}Ra and ^{228}Ra). Parallel 20 L samples at each pumping depth were collected from Niskin bottles and analyzed via alpha scintillation for ^{226}Ra to determine radium extraction efficiencies for the cartridges. These modified methods will allow for increased sample throughput, and hence higher spatial resolution for radium isotopes in the ocean. Such resolution will greatly improve the determination of oceanic vertical and horizontal mixing rates over small and large scales, which in turn can be used to calculate fluxes of TEIs into the ocean.

Keywords Radium · MnO_2 cartridge · GEOTRACES · Ocean mixing · In situ pumping

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Introduction

Naturally-occurring radium isotopes (^{223}Ra, ^{224}Ra, ^{226}Ra, and ^{228}Ra) have been used as tracers of submarine groundwater discharge and to estimate vertical and horizontal mixing rates in the open ocean [1–3]. For example, radium derived mixing rates have been used to determine upper ocean fluxes of trace elements like iron that control phytoplankton production and subsequent carbon dioxide draw down from the Earth's atmosphere [4, 5]. Analysis of radium isotopes in seawater typically begins with a preconcentration step, most commonly a slow (~1 L/min) filtration of 100–1,000s of liters through manganese-oxide (MnO_2) coated acrylic fibers [6, 7]. For open ocean profiles, this method requires the use of Gerard barrels or multiple CTD-rosette-Niskin bottle deployments, which is not practical as it consumes a large amount of station time aboard research vessels to collect water at depth. In preparation for the GEOTRACES international study of trace

elements and isotopes in the ocean (www.geotraces.org), we investigated different filter media types and MnO_2 coating methods capable of filtering at high flow rates (~8 L/min) and sorbing radium (and thorium) efficiently while deployed on an in situ pumping system. We describe an acrylic cartridge-based method and associated analytical procedure that produces high quality, full-ocean depth data that for the first time includes all four radium isotopes.

Experimental

MnO_2 filter media selection and preparation

Various types of MnO_2 impregnated adsorption media were tested to determine the cartridge type that most effectively binds radium and thorium. The radium absorption efficiency of each medium was tested as a function of high filtration rates due to the limited sample collection time onboard the research vessel and the large volumes needed for ^{228}Ra detection on a germanium gamma detector. The media tested included acrylic fiber and the following cartridge-based filters: wound acrylic [6], cellulose grooved CUNO (now 3M) [8], polypropylene Hytrex [9], and acrylic grooved CUNO. Detailed methods for the preparation of each cartridge type can be found in the references listed above. The method for the acrylic cartridges is described in detail below. Surface water from the Bermuda Atlantic Time Series site (31°40′N, 64°10′W) was collected in a 1,250 L tank, homogenized, and passed through the various cartridge types at flow rates ranging from 2 to 10 L/min. Extraction efficiency for radium was determined by comparing the cartridge activity to that of a discrete sample collected from the tank and analyzed for ^{226}Ra via pre-concentration on Mn fiber followed by gamma counting [6].

The results of the flow rate experiment were such that we selected the acrylic grooved CUNO for further testing, mainly involving different preparation methods to maximize the amount of manganese bound to the cartridge (12.7 cm length) thus maximizing the potential for a high radium and thorium extraction efficiency. The most common method for binding MnO_2 to acrylic media involves soaking in a heated solution (70–80 °C) of 0.5 M potassium permanganate ($KMnO_4$) [6]. Our first test applied this method and the end point for the cartridges was determined to be a dark brown color after multiple rinses with radium free water. The soaking time ranged from 15 to 45 min, and we monitored the temperature vigilantly as a rapid increase is an indication of an exothermic reaction with the acrylic. Also, if not monitored properly, the cartridges can be "overcooked", which makes them brittle. The other coating methods were stirred room temperature soakings (also 0.5 M $KMnO_4$) lasting twenty-four, forty-eight, and seventy-two hours. With the room temperature methods, we can prepare 20 cartridges in a large vat containing 40 L of $KMnO_4$ solution. Once the cartridges are removed they are allowed to drip dry overnight and the excess $KMnO_4$ is rinsed with radium free water until the effluent ran clear (about 20 L).

Cartridge extraction recoveries

Radium recoveries for the heated and room temperature cartridge methods were tested with surface seawater collected simultaneously into multiple 250 L containers from the dock in Woods Hole, MA. All samples were filtered at a flow rate of 1 L/min and acrylic fiber samples, which are known to quantitatively sorb Ra from seawater, were used as the reference sample for calculating cartridge Ra recoveries. The four types of coated cartridges (heated, 1, 2, and 3 day soak) and fiber were rinsed after the seawater filtration with radium free water in the lab to remove the salt for subsequent analyses. Excess water was also removed with filtered compressed air and counted immediately the RaDeCC counters for short-lived radium isotopes (^{223}Ra, ^{224}Ra) [10]. Measurements were also made 4 weeks and 2 months after sample collection to correct for supported ^{224}Ra and ^{223}Ra from ^{228}Th and ^{227}Ac, respectively. The acrylic cartridges were then placed in pre-weighed ceramic cups and placed in a muffle furnace with a ceramic lid at 820 °C for 48 h. The burn time for the cartridges was extended from 18 h (used for coated acrylic fiber) because of the increased media size and also to reduce the amount of ash produced. The ashed cartridges were homogenized and transferred to a pre-weighed polystyrene test tube. The final mass of the sample container was recorded to account for any loss of material during transfer. The samples were sealed with epoxy resin and analyzed on a high purity germanium detector (HPGe) after 1 month to allow for ingrowth of ^{214}Pb through ^{226}Ra decay. Peak areas were recorded at 352 keV for ^{214}Pb and 911 keV for ^{228}Ac to determine activities of ^{226}Ra and ^{228}Ra, respectively.

Preparation of MnO_2 acrylic cartridge standards

Preparing standards are essential in making precise measurements on the RaDeCC counting system. Since a new media and counting chamber were being used to extract radium isotopes from seawater, a set of Mn-cartridge standards were prepared to create an efficiency calibration for each RaDeCC counting system. Calibrated spikes were added to blank Mn-coated acrylic cartridges to cover the natural range of Ra activity in seawater. Stock solutions of ^{227}Ac (with ^{223}Ra in equilibrium), ^{226}Ra, and ^{232}Th (with daughters ^{228}Ra, ^{228}Th, and ^{224}Ra in equilibrium) were

Table 1 Detector efficiencies for radium adsorbed to MnO_2 acrylic fiber and acrylic cartridges analyzed via RaDeCC counters

RaDeCC detector	^{224}Ra efficiency fiber (%)	^{224}Ra efficiency cartridge (%)	^{223}Ra efficiency fiber (%)	^{223}Ra efficiency cartridge (%)
3	41 ± 1	42 ± 2	28 ± 7	32 ± 2
4	44 ± 3	44 ± 1	28 ± 8	30 ± 3
5	53 ± 6	47 ± 3	31 ± 10	33 ± 3
6	47 ± 5	48 ± 3	28 ± 11	35 ± 3
7	61 ± 2	42 ± 4	42 ± 8	31 ± 2
8	62 ± 4	51 ± 2	47 ± 12	38 ± 8

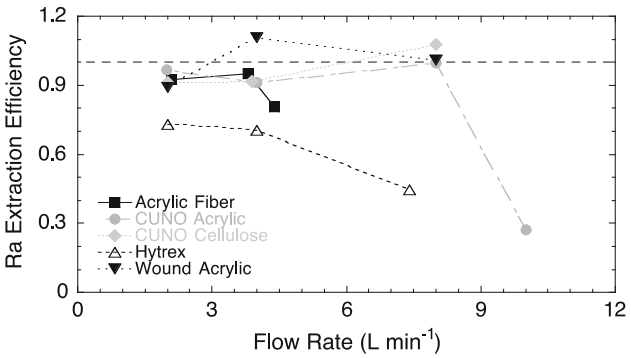

Fig. 1 Testing Mn-coated media for radium extraction efficiency from seawater with varying filtration rate

added directly to four 1 L zip lock bags filled with 300 mL of filtered radium free seawater (Table 1). The pH was adjusted to 7.5–8 using concentrated ammonium hydroxide. The Mn-coated blank cartridges were double bagged and soaked with a slow constant movement on a shaker table for 72 h. The cartridges were removed and allowed to drip dry for 24 h and the residue was collected and stored for later analysis. The cartridges were rinsed with 500 mL of radium free MilliQ water, and allowed to drip dry for another 24 h. Once installed in their filter holder, they were dried at 55 °C then rewetted with radium free water until the moisture weight was approximately 30 % of the cartridge weight. Standards were run frequently to ensure that the tracers and daughter products were quantitatively sorbed to the cartridge. The residual liquid from the radioisotope additions was plated and measured on a Canberra alpha detector, which indicated that Ra and Th was quantitatively sorbed to the cartridges.

Standard cartridges and acrylic fibers were also spiked and processed on HPGe detectors to determine detector efficiency at the energy of interest for ^{234}Th (63.3 keV), ^{226}Ra (352 keV) and ^{228}Ra (911 keV). Blank Mn-coated cartridges and acrylic fibers were spiked separately with ^{238}U (with ^{234}Th daughter in equilibrium), ^{226}Ra (NIST srm#4967A) and ^{232}Th (with ^{228}Ra daughter in equilibrium). The cartridges were ashed and transferred to vials with varying heights to create calibration curves as a function of packed ash height. Liquid standards were also prepared and processed on the gamma spectrometer for comparison with the ash standards to determine if activity was lost during the high temperature media burn.

Results and discussion

Media selection

Five different media types were tested with surface seawater during a GEOTRACES intercalibration cruise in 2008. The 3M grooved acrylic and 3M grooved cellulose cartridges had high radium recoveries (>95 %) up to 8 L/min, Hytrex cartridges averaged 70 % or less, while the acrylic fibers sorbed radium quantitatively up to 4 L/min (Fig. 1). Hytrex filters were noticeably lighter in color when they were mounted in the filter housings. This may be a sign of less MnO_2 binding to the polypropylene-based Hytrex filters and could explain the lower radium scavenging efficiencies. The cartridge media allowed for high filtration rates (12 L/min) with minimal backpressure on the pump whereas the pumps were not capable of rates higher than 4 L/min for the acrylic fiber. The geometry of the cartridge media is more suitable for high flow rate sampling/processing.

In an attempt to maximize radium sorption during filtration, a series of coating methods for the 3M cartridges was tested. The radium adsorption efficiency for the coated cartridges was calculated based on the averaged radium (^{223}Ra, ^{224}Ra, ^{226}Ra) acrylic fiber activity measured (assuming 100 % extraction efficiency) with a 1 L/min filtration rate. While all four coating methods had similar average Ra recoveries, the two-day room temperature soak had the highest radium recovery (84 ± 7 %). The others were lower but similar with the heated bath at 80 ± 7 % and the one and three-day soaks at 75 ± 8 and 76 ± 7 %, respectively (Fig. 2). Another important consideration when determining the coating method was the amount of ash remaining after combustion, which will determine how much of the sample can be packed into a typical well detector vial for gamma analysis. The 1 day soaked had 100 % of the test cartridges ash to a sample less than 10 g, which allows all of the sample to be measured in a single counting vial. The 2 day soak had 76 % of the cartridges ash to the acceptable size. The remaining test samples were analyzed in a larger counting vial with a less sensitive detector requiring longer analysis time. The heated and three-day cartridges had close to 50 % of the cartridges below the 10 g limit; while this suggests that these preparation methods led to more MnO_2 bound to the cartridge,

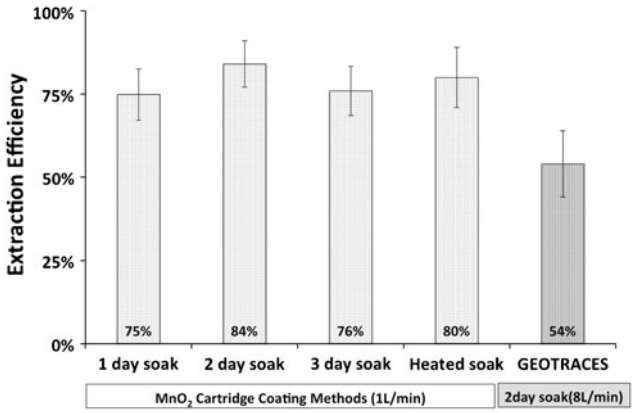

Fig. 2 Results of Mn-coating of the acrylic cartridges show similar extraction efficiency regardless of soaking time as tested with coastal seawater. Preliminary GEOTRACES results suggest a lower extraction efficiency for samples collected using the modified in situ pump in an open ocean setting

it did not result in a noticeably higher Ra recovery in the pumping tests.

MnO_2 cartridge detector efficiencies

A blank Mn-coated acrylic cartridge (labeled C–C) was spiked with 3 radioisotopes: 12 dpm of ^{234}Th (^{224}Ra daughter in equilibrium), 2 dpm of ^{227}Ac (^{223}Ra daughter in equilibrium), and 20 dpm of ^{226}Ra. To determine whether the radium activities were stable over time, the standard was counted repeatedly on six different RaDeCC counters from October 13, 2010 (soon after preparation) to November 26, 2010 (Fig. 3a, b). The results obtained were averaged daily, corrected for counter efficiency variability using a well-established acrylic fiber standard, and corrected for loss of ^{227}Ac through decay. The calculated activity of both isotopes remained stable (within uncertainties) suggesting that all parent radioisotopes were efficiently sorbed on the Mn-coated cartridge. For ^{223}Ra, there was significant run to run variability though this is likely due to the low activity of the ^{227}Ac standard used, which was chosen to match activities expected for samples from the field. Analyses averaged 85 net counts with a one-sigma counting error of 11 %. The ^{224}Ra had a higher spiked activity on the cartridge providing an average ~1,000 counts with a one-sigma counting error of 3 %. Cartridge standard C–C was run multiple times on the RaDeCC counters to determine ^{223}Ra and ^{224}Ra counting efficiency (Table 1). The ^{227}Ac spike that was added to the standard cartridge was corrected for activity loss due to decay. The average ^{223}Ra counting efficiency measured on the RaDeCC was between 30 and 38 %. These results were similar to the efficiencies measured using acrylic fiber standards (28–42 %). ^{224}Ra had higher counting efficiencies ranging between 42 and 51 % for the cartridges, while the acrylic fiber standard ranged from 41 to 62 %. The results indicate the different media have similar efficiency of detection on RaDeCC within the expected variability among counters.

For the long-lived radium isotopes (^{226}Ra and ^{228}Ra), samples are measured using gamma spectroscopy. To calibrate the detectors, blank cartridges were spiked with the appropriate isotope (287 dpm/g ^{226}Ra, 70 dpm/g ^{228}Ra as ^{232}Th), ashed, then transferred to polystyrene vials and sealed with epoxy resin. The four ^{226}Ra standards had varying ash weights (1.3, 3.1, 5.3, 6.4 g) to create a calibration curve for the expected range of ash volumes produced and packed to a similar density (1.5 g/cm^3). The detector efficiency decreased with increasing ash height from 21 to 16 % with an average of 18 % at 352 keV. Similar results were also obtained with acrylic fiber standards ranging from 19.1 to 14.3 % with an average of 16.6 %.

Four ^{228}Ra standards were made with a similar density and range of ash weights as the ^{226}Ra standards. Detector efficiencies measured at 911 keV ranged from 5.1 % with

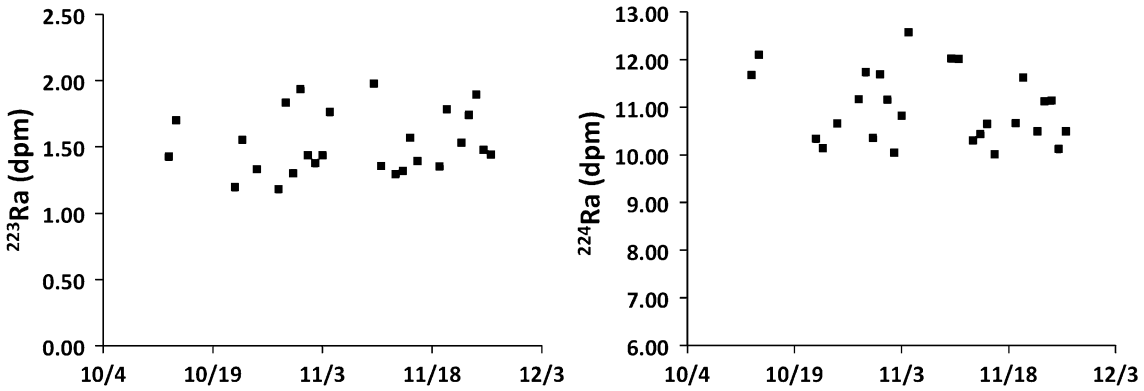

Fig. 3 Initial ^{223}Ra (*left graph*) and ^{224}Ra (*right graph*) measurements of cartridge standard C–C detector normalized. There is no measurable decrease in activity over time suggesting good adsorption of parent and daughter radionuclides in the spike

the smallest standard to 3.7 % with the largest. A set of acrylic fiber standards had similar efficiency calibration ranging from 3.9 to 5.8 %. An aliquot of the liquid spike (^{232}Th) was measured on the gamma spectrometer producing similar results (4.1–5.7 % efficiency). The acrylic and cartridge standards indicate there is no significant difference in detector efficiency and, most importantly, comparison with the liquid standard shows there is minimal loss of radium during 48 h of high temperature combustion.

Field results

Acrylic grooved cartridges were prepared and deployed on modified McLane in situ pumps to sample the radium quartet (^{223}Ra, ^{224}Ra, ^{226}Ra, ^{228}Ra) in high-resolution profiles during a U.S. GEOTRACES cruise (R/V *Knorr*, October 2010). Water was collected with 30 L Niskin bottles deployed in parallel with the in situ pumps and filtered on deck through acrylic fiber at less than 1 L/min to later determine radium extraction efficiencies via ^{226}Ra and the radon emanation method [11]. A total of 121 cartridge samples were collected from 8 stations over 18 days. The Mn bound acrylic cartridges filtered on average 1,620 L of water per sample during 4 h of pumping with an average flow rate of 6.6 L/min. In terms of ash volume, 87 % reduced to 10 g or less (Table 2). Radium analyses are still ongoing, but with close to a third of the samples completed, the cartridge samples have an average extraction efficiency of 54 %, significantly lower than we encountered during our initial tests with surface seawater. At present we cannot explain these differences though possibilities include water bypassing the filter at depth due to compression of the cartridge or use of cartridges that had less MnO_2 than our initial test batch. We are currently testing a modified cartridge preparation procedure that includes 24 h of presoaking in radium free water before immersion in the $KMnO_4$, which has produced a more uniform MnO_2 distribution. Preliminary results indicate that this simple modification to the method leads to higher radium extraction efficiencies.

To demonstrate that these methods lead to oceanographically consistent radium distributions, we present results from the GEOTRACES cruise station 5 (31°00′N, −22°00′W). We chose this station to highlight since there

Table 2 Ash weights measured from combusted Mn-coated acrylic cartridges used on the GEOTRACES Atlantic cruise

	0–3 g	3–6 g	6–10 g	>10 g
Number of samples	21	43	41	16
Mean (g)	1.7	4.9	7.4	12.4
Standard dev	0.7	0.8	1.0	3.4

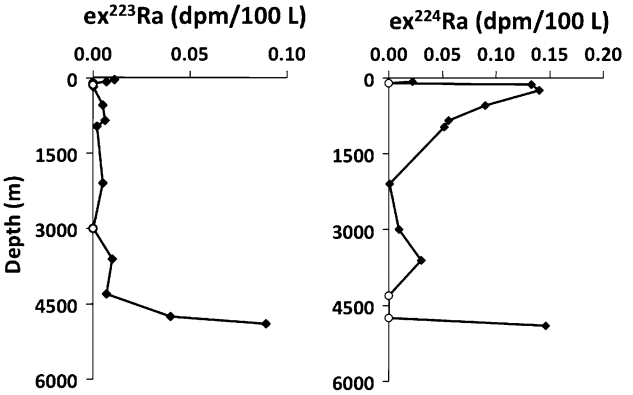

Fig. 4 Excess ^{223}Ra (corrected for ^{227}Ac) shows near background levels with an increase near the seafloor (4900 m) due to diffusion from bottom sediments. Excess ^{224}Ra (corrected for dissolved ^{228}Th) shows a source of radium near the bottom. Elevated surface activities for ex^{224}Ra may be due to contributions from particulate ^{228}Th. Data points that were found to be below the detection limit of the method are plotted as zero values (*open circles*)

is historical data for long-lived radium collected near the same location, to which comparisons can be made. Additionally, for the first time we present full-ocean depth water column profiles for the short-lived radium isotopes. For excess ^{223}Ra (measured ^{223}Ra minus that supported by ^{227}Ac decay on the cartridge), we found near background levels from the surface to 4,000 m with an increase near the seabed, likely due to diffusion of radium from the sediments (Fig. 4). Excess ^{224}Ra shows a source near the surface and bottom, with the mid depths of the profile near background. The bottom source indicates diffusion from the sediments as with ^{223}Ra. Results from the surface ^{224}Ra will need to be validated due to the relatively short half-life of the isotope and distance for advection to occur from the nearest coast (∼450 km). The ^{228}Ra profile is consistent with typical open ocean distributions with a source in the

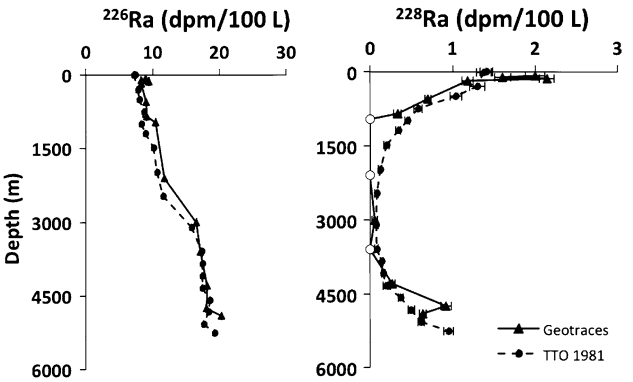

Fig. 5 The long lived Ra isotopes from GEOTRACES as compared with data collected from a nearby Transient Tracers in the Ocean (TTO) program station (33°11′N, −21°44′W) collected in 1981. Data points that were found to be below the detection limit of the method are plotted as zero values (*open circles*)

surface ocean (coastline) and near the bottom (diffusion from sediments) with low activity in the mid water column due to decay during slow vertical mixing (Fig. 5). The depth distribution of ^{226}Ra as compared to a profile collected from a cruise in 1981 [12] shows identical activity and shape.

Conclusions

Five different Mn-coated cartridges were evaluated for determining the extraction efficiency for naturally-occurring radium isotopes in seawater. The Mn-coated acrylic grooved cartridge made by 3M performed the best in not only radium adsorption tests of surface seawater but, when ashed, yielded a manageable sample size for radium analysis via gamma counting. Different coating methods were tested with a procedure involving a 48 h soaking period having acceptable radium extraction efficiencies with a reasonable quantity of ash. A MilliQ water presoak is recommended to improve MnO_2 uptake by the cartridge. Standard solution spiked had similar counting efficiencies among the different Mn-coated media (fiber vs. cartridge) for both RaDeCC and gamma spectrometry. The new cartridge collection methods and counting procedures were successful in producing both short and long-lived radium profiles that are consistent with our understanding of radium cycling in the open ocean. This new collection method will aid in determining high-resolution vertical and horizontal mixing rates and distributions of trace elements and isotopes in the ocean.

Acknowledgments The authors would like to thank Wendy Plessinger, Meagan Gonneea, Crystal Breier, and Stephanie Owens for analytical and technical support. This study was funded by NSF grants OCE 0925158 and OCE 0751461.

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