GEOTRACES Intercalibration Report
Radium Isotopes and 228-Thorium on GP16

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This report provides evidence in support of the data quality for radium isotopes and 228-thorium collected by our laboratories during the U.S. Pacific GEOTRACES GP16 cruise (Oct.-Dec. 2013). Since there are no crossover stations available to date, we will outline the results of our participation in a Proficiency Test for ^{223}Ra, ^{224}Ra, ^{226}Ra, ^{228}Ra, and ^{228}Th in June 2008 (23 laboratories participating, Charette et al., 2012). Further, for ^{226}Ra, we compare our results with historical data collected along the same section. There are no historical data for ^{228}Ra and ^{228}Th nor the two short-lived Ra isotopes ^{224}Ra and ^{223}Ra.

The intercomparison study was divided into two parts involving the distribution of: (1) samples collected from four marine environments (open ocean, continental slope, shelf, and estuary) and (2) a suite of four reference materials prepared with isotopic standards (circulated to participants as 'unknowns'). The two main laboratories participated separately; Woods Hole Oceanographic Institution (WHOI) was assigned identification number 13 and the University of South Carolina (SC) was lab number 12. Our colleague Doug Hammond at the University of Southern California was measuring ^{227}Ac on our Mn cartridges and therefore provided key data needed to quantify excess ^{223}Ra. He is lab number 5 in the intercomparison study.

We participated in a second inter-comparison exercise conducted during May 2011 using surface seawater of the Asian coastal region. Analyses included the four Ra isotopes and ^{228}Th. One sample set was collected in the coastal region of the Yellow Sea near Qingdao, China and in Tolo Harbor of Hong Kong. The details of our performance in that exercise are not included here but can be found in Du et al. (2013) (WHOI is lab #732, SC is lab #821).

There are four distinct sample types that were collected on the cruise. Manganese cartridges are deployed on McLane in situ pumps, which concentrate between ~1200-1800 L of Ra and Th isotopes from the depth of interest (Henderson et al., 2013). Parallel, Niskin bottle samples are collected at each depth for discrete ^{226}Ra and ^{234}Th analysis; these data are used to calculate the respective Ra and Th scavenging efficiencies of the Mn cartridges. For the Pacific dataset, the average Ra cartridge scavenging efficiency was 66±17% while the Th efficiency was 53±20%. Due to the long counting times involved for the low levels of ^{228}Ra in the Pacific Ocean, at this time we are only reporting the data for the eastern half of the GP16 transect as well as selected depths within the hydrothermal plume on along the western half. A third sample type is Mn fiber placed in a mesh bag and suspended in the upper ~3m of the water column for 24 hours at each station. Since the precise Ra preconcentration volume for these Mn fiber samples is not known, ^{228}Ra was approximated using the corresponding near surface Niskin bottle ^{226}Ra. The two short-lived Ra isotopes, ^{223}Ra and ^{224}Ra, were not measured on the mesh bag samples. The effective volume scavenged during the 24-hour deployment averaged 1000±560 L. Finally, QMA filters were analyzed for ^{228}Th at all McLane pump depths.

^{226}Radium

Methods

The McLane large volume in situ pump (WTS-LV) was modified to filter seawater through two ~12 cm long manganese oxide coated ribbed cartridges placed in series. The second Mn cartridge is used only for determining Ac scavenging efficiency. Eight pumps were deployed simultaneously and were programmed to run for four hours at a rate of 8L/min with total volumes ranging between 1200-1800L of seawater. At high flow rates (>1L/min) the radium extraction efficiency from the cartridge is less than 100%. The second sample type was collected from a 30L Niskin mounted directly above the WTS-LV (>1000 m) or on a CTD Rosette (<1000 m). These samples (15-25 L) were gravity filtered through 15 g of manganese oxide impregnated acrylic fiber at approximately 0.5L/min. Since this method quantitatively removes radium from seawater, these small volume samples were analyzed for ^{226}Ra to determine the individual extraction efficiency of each cartridge for all isotopes of radium. The filtrate was collected inside of a graduated rigid sided container and the volume was recorded. A mass was also obtained by using a hand held digital balance. The third sample type was the Mn fiber placed in mesh bags and hung over the stern of the research vessel while it was on station. The "passive filter" deployment ranged anywhere from 8 to 54 hours, which was dependent upon the time spent at a sampling station.

Initial ^{224}Ra and ^{223}Ra measurements were conducted on the ship and back in the lab (described below). At the completion of these measurements, the Mn cartridges and mesh bag fibers were placed in a tared ceramic vessel with lid and combusted at 820°C for 48 hours. The sample ash was homogenized, and packed to a consistent density of 1.5g/ml (ash weight/volume) within a polystyrene counting vial. The sample ash was then sealed with 1.5ml of a two-part epoxy from West Marine (West System 105, 205) and stored for 30 days to allow for secular equilibrium between ^{226}Ra and its progeny ^{214}Pb. The cartridge ash was counted in a high-purity germanium well-type gamma spectrometer to measure ^{226}Ra activities at 352keV (van Beek et al. 2010). Mn cartridge samples were counted both at WHOI and in the underground lab at Modane, France in collaboration with our French GEOTRACES colleagues Pieter van Beek and Jean-Louis Reyss. Mesh bag Mn fiber samples were analyzed at SC. Each High Purity Germanium detector was calibrated using a NIST-certified ^{226}Ra standard (SRM#4967A). The standard solution was applied to Mn fiber or Mn cartridges that were ashed and prepared for counting in the same manner as the samples. A range of four ash heights was created to determine the counting efficiency as a function of sample volume in the counting vials. These reference standards were distributed to SC and Modane to ensure intercalibration among the three laboratories. Counting uncertainties are calculated as 1-sigma.

The Mn fiber from the Niskin bottles were rinsed with deionized water back at WHOI, partially dried, and sealed within a fiber holder after being flushed with helium equivalent to 30 column volumes. Samples were stored for a minimum of 12 days and analyzed for ^{226}Ra via ^{222}Rn ingrowth using alpha scintillation counting (Key et al., 1979). Samples were counted for 180 minutes, which resulted in counting uncertainties of ~3% dependent upon ^{226}Ra content on the fiber and sample volume. The method was calibrated using NIST ^{226}Ra

(20 dpm) sorbed to Mn fiber and analyzed in the same manner as the samples. Standard reproducibility was 2-3% on average. Final sample measurement error was based on counting uncertainty, standard deviation of the Lucas cell background, and the standard deviation of the detector efficiency. The average error measured for the Niskin bottle Mn fibers for the Pacific GEOTRACES cruise ranged between 3-5%. These are the ^{226}Ra values presented our report.

Participation in Intercalibration

The WHOI and SC intercalibration results for ^{226}Ra are shown in Table 1. Both laboratories results fell within the 95% confidence interval with the exception of one SC sample (Station 3), which had a known problem with the flow meter (Charette et al., 2012).

Table 1. Summary of ^{226}Ra (dpm/100L) results from the WHOI and SC laboratories for GEOTRACES inter-calibration cruise aboard the R/V Knorr 2008.

^{226}Ra	*(Open ocean)*	*(Slope)*	*(Shelf)*	*(Estuary)*
	Station 1	***Station 2***	***Station3***	***Station 4***
Participating Laboratories	12	13	13	11
Median	7.28	9.7	16.5	17.6
95% Conf. Interval	7.1-8.27	8.2-12.3	11.6-24.3	14.5-21.5
WHOI Z score	0.60	0.69	0.26	0.80
WHOI results	7.28	8.4	15.1	14.5
SC Z score	0.60	0.40	1.15	0.77
SC results	7.28	9.1	10.4*	14.6

***There were problems with the flow meter used to record the volume of this sample.**

Historical Comparison

The ^{226}Ra activities determined during the US. GEOTRACES GP16 cruise range from 5.77 ± 0.17 dpm/100 L to 34.86 ± 1.28 dpm/100 L. The ^{226}Ra activities increase from the surface to the deep ocean similar to previous studies for this and other ocean basins (*e.g.* Broecker et al. 1976; Ku et al. 1980; Chung 1980; Chan et al. 1976). Of particular relevance to our GP16 dataset are two expeditions, which were conducted in the subtropical Pacific Ocean near the East Pacific Rise: the SIO Expedition SCAN in 1969 and the SIO Expedition SOUTH-TOW in 1972 (Chung 1980; Chung and Craig 1973). For these studies, seawater samples were collected using Niskin bottles and stored in 20-l glass carboys until ^{222}Rn reached secular equilibrium with ^{226}Ra. The ^{226}Ra activities were then determined *via* ^{222}Rn in an alpha-scintillation system using cylindrical Lucite counting cells (Damon and Hyde 1952; today called "Lucas cells"). Despite the additional Mn fiber preconcentration step used

during GP16 (^{222}Rn emanation from adsorption onto MnO_2 fiber, Moore et al. 1985), the vertical profiles of ^{226}Ra activities show a very good agreement (Figure 1). Note that the uncertainties of surface samples with low activities in the GP16 dataset have been significantly reduced compared to the SIO dataset. Overall, the ^{226}Ra activities measured during the GP16 cruise also agree well with the ^{226}Ra activities determined more widely in the Pacific Ocean during the GEOSECS program (Chan et al. 1976; Ku et al. 1980), noting that deep water ^{226}Ra in this ocean basin generally increases from south to north. Additionally, the ^{226}Ra / Silica ratios throughout the water column show a consistent pattern with a higher ^{226}Ra / Silica ratio close to the bottom due to sediment inputs in agreement with Chung (1980) (not shown).

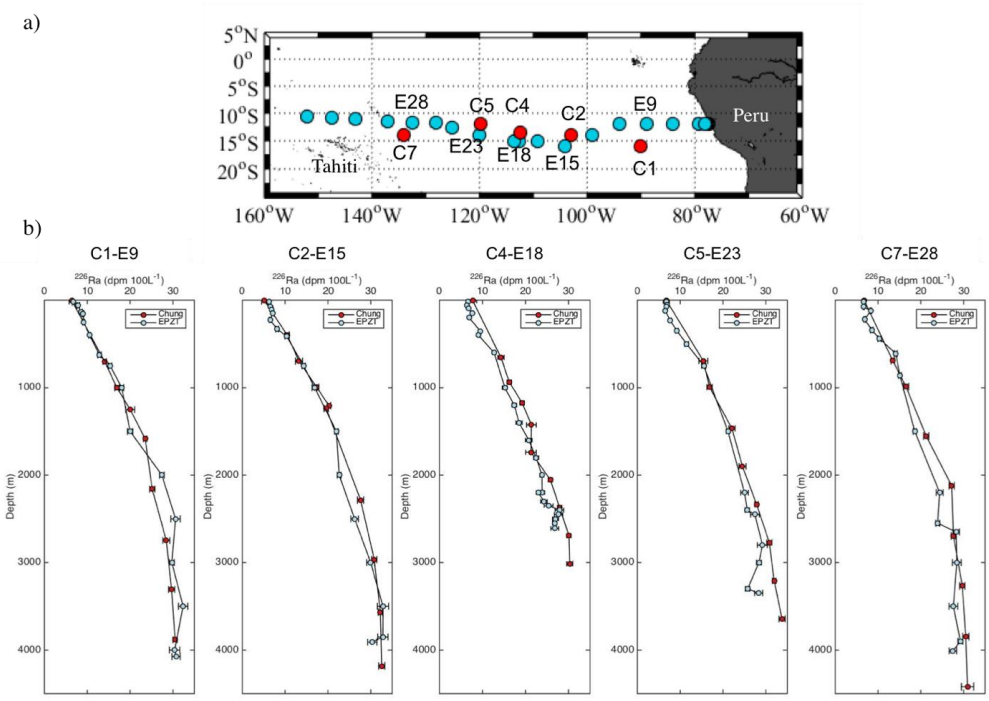

Figure 1: 1a) Station locations for U.S. GEOTRACES GP16 cruise (blue) and those for the SIO Expedition (Red; Chung 1980; Chung and Craig 1973). 1b) Comparison of water column ^{226}Ra activities for the stations nearest to the SIO study (dpm/100 L). Note that the station order in (b) is for stations from east to west.

^{228}Radium

Methods

Sample analysis for ^{228}Ra was performed on cartridges and mesh bag Mn fibers collected during the Pacific GEOTRACES cruise. Sample preparation and analysis is the same as for ^{226}Ra (combustion followed by gamma counting). Radium-228 is quantified from gamma lines at 338, 911, and 968 keV (^{228}Ra daughter ^{228}Ac).

The reference material for ^{228}Ra was prepared gravimetrically from a greater than thirty-year old source of thorium nitrate powder (45% ^{232}Th by weight). The powder was weighed and dissolved in 7N nitric acid. An aliquot from this solution was spiked with ^{229}Th (SRM#4328) and analyzed on a Finnegan Neptune high-resolution multi-collector ICP-MS, which confirmed the ^{232}Th activity of the standard solution. To ensure that the ^{228}Ra daughter was in secular equilibrium with ^{232}Th, ^{228}Ra was measured via MC-ICP-MS using ^{226}Ra (SRM#4967A) as the internal standard prepared for analysis via the method of Foster et al. (2004). Spiked cartridge and fiber ash was analyzed at the University of South Carolina and the underground gamma counting facility in Modane, France for cross calibration purposes. The errors are reported as 1-sigma and were propagated from the gamma counting uncertainty and the Mn cartridge scavenging efficiency error.

Participation in Intercalibration

The ^{228}Ra results for our labs from the GEOTRACES intercomparison exercise are shown in Table 2. All results fell within the 95% confidence interval (CI) except for station 2 (WHOI), which 0.1 dpm/100L below 95% CI range and station 3 (SC; volume error).

Table 2. ^{228}Ra (dpm/100L) results from the WHOI and SC laboratories for GEOTRACES inter-calibration cruise aboard the R/V Knorr 2008.

^{228}Ra	*(Open ocean)*	*(Slope)*	*(Shelf)*	*(Estuary)*
	Station 1	***Station 2***	***Station3***	***Station 4***
Participating Laboratories	11	11	11	11
Median	2.99	14.9	36.4	58.4
95% Conf. Interval	2.03-3.24	13.2-16.3	34.2-39.6	52.4-63.2
WHOI Z score	-0.48	0.86	1.12	0.54
WHOI results	3.03	13.1	32.9	55.2
SC Z score	-0.3	-0.86	1.9	-0.4
SC results	2.94	16.1	30.4*	59.9

***There were problems with the flow meter used to record the volume of this sample.**

^{223}Radium, ^{224}Radium

Methods

The two short-lived Ra isotopes were measured on the Mn cartridges only. The Mn cartridges were rinsed immediately after collection onboard the R/V Thompson with fresh water, partially dried, placed in a closed looped system, and measured on Radium Delayed Coincidence Counting systems (RaDeCC) (Moore and Arnold 1996). Samples were counted

for 6 hours with a purging step after 3 hours to minimize the buildup of ^{222}Rn decay of ^{226}Ra. A second analysis (also 6 hour counting) was conducted on the RaDeCC after 25 days to measure the ^{224}Ra supported by ^{228}Th. A third and final RaDeCC count (12-24 hours) was performed after ~80 days to quantify the ^{223}Ra supported by ^{227}Ac. The third measurements made on the cartridges were split between WHOI, SC, and U. Southern California). Mn cartridge standards were prepared as follows: seawater was filtered for particulates and Ra/Th/Ac using an Mn fiber. The seawater was spiked with ^{227}Ac or ^{232}Th with daughters in equilibrium and circulated across an Mn cartridge (^{227}Ac) or soaked for several days (^{232}Th). The standards were analyzed several times on each of the RaDeCC systems during the cruise and back in the lab. After the cruise they were shared with the Moore and Hammond labs to be run on their RaDeCC systems. The errors are reported as 1-sigma and were propagated from the RaDeCC counting uncertainty for parent and daughter as well as the Mn cartridge scavenging efficiency error.

Participation in Intercalibration

The short-lived Radium isotopes were collected for 4 stations on the GEOTRACES inter-calibration cruise aboard the R/V Knorr. The results reported for $^{223}Ra_{xs}$ and $^{224}Ra_{xs}$ have been corrected for supported radium from ^{228}Th and ^{227}Ac during the first, second, and third counts on the RaDeCC but also decay corrected to the time of sample collection. All samples measured at WHOI and SC fell within the 95% confidence interval.

Table 3. Radium isotopes as measured by WHOI and SC for GEOTRACES inter-calibration exercise. $^{223}Ra_{xs}$ and $^{224}Ra_{xs}$ (dpm/100L) results are excess values after correction of total radium for supported radium from ^{228}Th and ^{227}Ac.

	$^{223}Ra_{xs}$	$^{223}Ra_{xs}$	$^{223}Ra_{xs}$	$^{223}Ra_{xs}$	$^{224}Ra_{xs}$	$^{224}Ra_{xs}$	$^{224}Ra_{xs}$	$^{224}Ra_{xs}$
	Open ocean	***Slope***	***Shelf***	***Est.***	***Open ocean***	***Slope***	***Shelf***	***Est.***
	Station 1	***Station 2***	***Station 3***	***Station 4***	***Station 1***	***Station 2***	***Station 3***	***Station 4***
Number of Labs	8	9	12	11	5	7	12	10
Median	0.05	0.05	1.34	6.2	3.4	1.4	14.5	67.3
95% Conf. Interval	0.03-0.08	0.03-0.07	0.87-1.77	4.5-10.3	0.16-8.61	0.7-3.3	13.0-16.8	62.6-74.8
WHOI Z score	0.00	1.00	0.43	0.19	0.41	0.73	-0.48	0.03
WHOI results	0.05	0.03	1.12	6.2	2.44	1.0	15.6	68.2
SC Z score	0.5	0	0.92	0.16	-0.04	0.45	0.65	0.59
SC results	0.04	0.05	0.87*	6.3	3.83	1.3	13.0*	64.5

***There were problems with the flow meter used to record the volume of this sample.**

A second radium inter-calibration exercise, a laboratory proficiency test, involved the distribution of six reference materials (labeled C, E, I, H, F, J) prepared by the IAEA-

Environment Laboratories in Monaco. The reference standards were provided to laboratories as unknowns and had to include the activities of their long-lived parents because of their short half-lives. The reference materials included ^{227}Ac, ^{232}Th, and a mixed ^{227}Ac+^{232}Th loaded on Mn-Fibers in an activity that closely corresponds to natural samples. After preparation, the reference material was measured repeatedly to show stability (Scholten et al. 2010). The samples were circulated from a main lab to participating groups and then returned to the original lab after analysis to ensure that was no significant change in the reference material. The laboratory ID remained as 13 for the Woods Hole Oceanographic Institution. For the six reference materials measured for ^{224}Ra, all of the activities reported were within 10% of the assigned value from IAEA. For ^{227}Ac, the Mn fiber standard was shown to be unstable as evidenced by a ~20% decrease in count rate within 2 months after preparation.

^{228}Thorium

Methods

Particulate samples were collected on a 142-mm diameter quartz fiber filters (Whatman QMA) deployed on a modified McLane pump. Sample volumes were measured by a flow meter mounted after the filter with an average filtration rate of 4.7L/min and a total of ~1000 L filtered per deployment. When the pumps were retrieved, the remaining water in the filter housing was vacuum filtered through the housing to prevent loss of particles during retrieval. Thorium-228 was measured directly on the QMA filters using the RaDeCC after being mounted inside the counting chamber. This was specially designed for analysis of particulate ^{228}Th via RaDeCC (Maiti et al., 2015). The isotope was measured through its daughter, ^{224}Ra ($t_{1/2}$ = 3.66 days), at least four weeks after sampling to allow for the development of secular equilibrium between ^{228}Th and ^{224}Ra. We note that this method can detect adsorbed ^{228}Th that can release ^{220}Rn; this result should be considered a lower limit, as there may be an additional component tied up in phases that cannot release its radon daughter product. Samples were dampened with 5 mL of Milli-Q (EMD Millipore) water, counted for approximately 24 h, and then dried in a 55 °C oven overnight for subsequent sample analysis by other participating laboratories. Analytical uncertainties are 1-sigma based on the net counts recorded over the counting interval.

Dissolved ^{228}Th was measured on cartridges and passive Mn fibers collected on the R/V Thompson. Sample preparation, analysis, and calibration procedures are the same as for ^{224}Ra (freshwater rinse, partial dry, measure on RaDeCC). The reference standards (cartridge and fiber) that were made for ^{224}Ra were routinely measured on the ship and back in the laboratories of all participants. The final dissolved ^{228}Th data are corrected for the Th cartridge scavenging efficiency, which is determined from the ratio of ^{234}Th on the cartridge ash (gamma counting as above) and ^{234}Th in the same Niskin bottles as the discrete ^{226}Ra analyses (Buesseler IDP2017). The measurement errors are reported as 1-sigma, and include counting uncertainty as well as the Th scavenging efficiency error.

Standard Preparation

To determine the efficiency for the filter geometry directly in the RaDeCC system, we added

the ^{232}Th standard to a filter collected at 1200 m at station 13 (14.00°N, 99.00°E) of GP16 that had an estimated POC concentration of 0.137 µM and an initial ^{228}Th activity of 0.006 dpm/100 L. The filter was spiked in a series of 4 additions ranging from 0.15 to 6.65 dpm and was prepared for analysis in the same manner as samples and analyzed on two of our RaDeCC detectors after each spike addition. More details on the method and standard preparation for ^{228}Th can be found in Maiti et al., 2015.

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