Activity of actinium-227 from water samples collected on Leg 2 (Hilo, HI to Papeete, French Polynesia) of the US GEOTRACES Pacific Meridional Transect (PMT) cruise (GP15, RR1815) on R/V Roger Revelle from Oct-Nov 2018

Website: https://www.bco-dmo.org/dataset/941157
Data Type: Cruise Results
Version: 1
Version Date: 2024-10-23

Project
» US GEOTRACES Pacific Meridional Transect (GP15) (U.S. GEOTRACES PMT)
» U.S. GEOTRACES Pacific Meridional Transect: Measurements of Actinium-227 to Trace Solute Transport (PMT Actinium-227)

Program
» U.S. GEOTRACES (U.S. GEOTRACES)

Contributors	Affiliation	Role
Hammond, Douglas E.	University of Southern California (USC)	Principal Investigator
Kemnitz, Nathaniel	University of Southern California (USC)	Student
Rauch, Shannon	Woods Hole Oceanographic Institution (WHOI BCO-DMO)	BCO-DMO Data Manager

Abstract
Actinium-227 (227Ac) was captured on commercial water filters impregnated with manganese dioxide (MnO2) and placed downstream of the filters in submersible pumps deployed on GEOTRACES expedition GP15, aboard R/V Roger Revelle, in collaboration with groups from Woods Hole Oceanographic Institution (WHOI) and University of South Carolina who measured radium isotopes on the same cartridges. The activity of 227Ac was measured using RaDeCC (Radium Delayed Coincidence Counter) and used to calculate the concentration of dissolved 227Ac along the transect by PI Douglas Hammond and graduate student Nathan Kemnitz. Data have been summarized and will be submitted in a publication to be submitted to JGR Oceans, along with a companion data set for 227Ac, 228Ra, and 210Pb in sediments. This dataset has been used to evaluate deep ocean solute transport. This dataset includes data from Leg 2 of the cruise (RR1815). Leg 1 data (RR1814) are available in a separate BCO-DMO dataset.

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Coverage

Spatial Extent: **N**:17.5 **E**:-151.986 **S**:-20 **W**:-152.029
Temporal Extent: 2018-10-27 - 2018-11-23

Methods & Sampling

227Ac Methods for Geotraces GP15

Note about figures: The following methods are also described in the attached PDF named "Methods for Geotraces GP15 227Ac Analysis" (see Supplemental Files). Figure numbers refer to figures in the PDF.

Overview: The decay chain for 235U is shown in Fig. 1. This illustrates both how 227Ac is formed in the ocean, and also the decay scheme of its progeny that are used for its measurement. McLane Pumps were deployed at various depths on the GEOTRACES GP15 cruise aboard the R/V Revelle. Typically, a total of about 1500 liters (L) of water was pumped through two filter paths for the collection of particulates, with about half going through a QMA glass Fiber filter (1-micrometer (µm)) and the other half passing through a stack of filters with the smallest a PES Supor800 filter (0.8 µm). The effluent from the filters was combined and directed to a set of commercial acetate or acrylic cartridges that had been impregnated with MnO2. The approximate flow rate was 6 L/minute during the pre-set pump time of 4 hours. Ac, Ra, and Th in seawater were sorbed as water was pumped through them, although at this high flow rate, the sorption efficiency was less than 100% for each of these isotopes. Presumably, 231Pa, the 227Ac parent was also sorbed because it is very particle reactive. Analyses of Ra on these cartridges have been made by collaborating groups (M. Charette at WHOI and W. Moore at U. So. Carolina).

Two cartridges were used in series (A and B), allowing the 227Ac extraction efficiency from seawater at high pump rates to be calculated (see below). After extracting 227Ac in the field, it was analyzed in the lab. A stream of He passed through these fibers to transport the 219Rn progeny from 227Ac decay into a Radecc counter (Moore and Arnold, 1996). Radecc has circuitry that can distinguish decays of 219Rn, 220RRn, and 222Rn by opening windows following detection of an alpha decay. If a second decay is observed in these windows produced by a short-lived Po daughter, its arrival time can be used to distinguish which Rn may have produced the initial signal.

Considerable time was spent on confirming the accuracy of the Radecc method, including preparation of new standards for 227Ac and evaluating standard stability, effects of geometry, flow rate used for analysis, and "crosstalk" that has been observed for Radecc channels measuring 219Rn and 220Rn (descendants of 227Ac and 228Ra). Sections below show details of data reduction and calibration.

Data Processing Description

RaDeCC Data Reduction: The instrument opens a two-stage window when an alpha decay is detected. The first stage (219 window) spans 0.01 to 5.60 ms and the second (220 window) spans 5.61 to 600 ms. Any subsequent decays occurring in each window are recorded. Decays of 219Rn lead to decays of 215Po that primarily occur in the 219 window and decays of 220Rn lead to decays of 216Po that primarily occur in the 220 window. The total record for events observed in successive 10-minute intervals are stored in a text file. A Matlab program was written to read these files, correct the values in each window for random decays of other isotopes, and for decays of 219 that occur in the 220 window plus decays of 220 that decay in the 219 window. The program plots the corrected activity vs. time. Random events resulting in chance coincidence in each window build up over time, and when these become large enough to dominate the window signal, the count is terminated. Water evaporating from the wet sample can condense in the detector and reduce efficiency during the count. If air leaks into the helium counting matrix, efficiency can also drop. These decreases in efficiency can be evaluated from the window signals vs. time, and the count is terminated when a decrease in counting rate appears to pose a problem. For GP15 samples, each count was 120 to 350 minutes, depending on the behavior observed. Anomalous signals indicating counter noise can also be detected and removed (rare).

Computations have been described by Moore and Arnold (1996), although two corrections were made for this work. For each channel:

$cc\# = R^2 t_g/(1-Rt_g)$

where cc# is chance counts for the window # and t_g, is the window open interval;

R = random single events = BC - AC

where BC = total count rate and AC = sum of 219 and 220 window count rates;

$cc219 = (t1/tg) R^2(tg)/(1-R*tg)$

$cc220 = (t2/tg) R^{2(}tg)/(1-R*tg)$

where t1 and t2 are the duration of the 219 and 220 windows and tg is t1+t2. This corrects the algorithm with the addition of the first term on the right of the cc219 and cc220 expressions above. It makes little difference for low activity samples, but becomes significant at high count rates.

The second change was to solve simultaneous equations to correct for 219 in the 220 window and 220 in the 219 window from the signals after correction for chance counts:

Final 219 cpm = corr219 - 0.0288*(corr220)

Final 220 cpm = corr220 - 0.1279*(corr219)

With the constants in the equations above determined from the window durations and the Po daughter decay constants.

The matlab routine calculates uncertainties as the standard deviation of the means of the 10 minute counting interval lines.

Geometry and Standard Calibration: Two types of sample geometry have been used extensively by the community. The traditional one was developed by Moore (1976) and uses acrylic fibers coated with MnO_2, housed in an acrylic tube about 200 cc in volume (identified here as MF geometry). The second type (used in Geotraces sampling by several groups) uses a commercial water filter coated with MnO_2, housed in a commercial filter holder (~450 cc, identified here as CC geometry). A standard solution of 227Ac obtained by our collaborators at WHOI was obtained from Eckert and Ziegler, diluted, and sent to USC. This solution was used to prepare standards in the Geotraces CC geometry by adding an aliquot of spike to about 1 L of Ra-free seawater (prepared by passing through Mn-fibers in a MF cartridge). The spiked seawater was then passed through a cartridge 5 times at about 1 L/minute to ensure all Ac was sorbed. The residual seawater was later checked for 223Ra activity to be sure no Ac had remained in the solution or on the walls of the bottle. No activity was found. Multiple standards were prepared, but standardization was primarily with Std K-21. In addition, standards were prepared on acrylic fibers (MF geometry). One historical standard prepared from a calibrated solution of dissolved urananite (std 27) has been in use in our lab and was run regularly during the analysis of GP15 samples to ascertain any deterioration of detectors during this time. The relative efficiency of our 6 detectors remained constant while GP15 samples were being analyzed.

Radon Release Factor: 227Ac standards in the MF geometry typically decline by 10-20% with time, over a few months, and then become stable. This is evidence that as the initially sorbed 223Ra decays and is replaced by atoms produced by 227Ac sorbed to the fiber, some 219Rn must be recoiled deeper in the fibers, hindering its escape during the 3.96 s half-life of these atoms. This decline with time is not seen in CC geometry standards, as we have found these to be stable for many years. However, we have found that samples in the CC geometry release 219Rn about 30% more slowly than the initial release rate of standards in the MF geometry, resulting in lowered counting efficiency, when counters are run at our normal He flow rate.

Flow Rate Effects for Radecc: The CC geometry has been found to be much more sensitive to flow rate than the MF geometry (Fig. 2). It is critical for the CC geometry to keep flow rate in the normal range to obtain consistent results.

Channel Crosstalk: Signals in the 219Rn channel are created by high activity in the 220Rn channel (Fig. 3). The effect remains after chance count correction and also correcting the 219 counts for contributions from decay of the 216Po that is expected in the 219 window. Scholten et al. (2010) had previously noted this feature. We have confirmed it, and found it seems to be independent of channel identity. There does not seem to be an effect of high 219Rn on the 220Rn channel. The cause of the signal is likely from the fraction of decays of 216Po that occur after the 220 window is closed. The result is that the gate windows re-open, and some additional events are captured. The effect depends on the activity of 220Rn and can be removed by an empirical algorithm:

220 cpm: Crosstalk in 219 cpm

0-2: no correction

2-6.6: 0.0358*(220cpm) - 0.012

>6.6: 0.06433*(220cpm-6) + 0.0358

For samples from GP15, this effect was generally negligible.

Cartridge Sorption Efficiency: When cartridges are in series and cartridge quality is uniform, the sorption efficiency can be determined from the ratio of activities on the two cartridges, A_B/A_A:

Eff = 1 - A_B/A_A

However, most GP15 samples were run with A cartridges prepared at WHOI and B cartridges prepared at USC. The USC cartridges were used in both positions at station 37, and found to be 65% efficient. This is similar to our previous observations in the South Pacific (65%) and Arctic (62%), as well as the 65% observed by Geibert (2002) at similar flow rates and cartridge size. However, A cartridges were usually less efficient than B cartridges and somewhat more variable, averaging 23%. Consequently, total sample activities were calculated as (A activity) + (B activity)/(0.65), when two cartridges were used for sampling. In the upper water column, most sampling used only 1 WHOI cartridge, and there the activity was calculated as (A activity)/(0.23). The uncertainty in efficiency is difficult to evaluate, but appears to be about 0.05, based on data previously collected in the South Pacific. This introduces an uncertainty of 11% in the calculation of sample activity when A and B cartridges were used, and 20% if only one cartridge was used. Interestingly, the sorption efficiency for Ra on USC cartridges was 80%, higher than for Ac. Data based on a single cartridge has been flagged with 2, probably ok, but with greater uncertainty than samples collected with paired cartridges.

227Ac Concentration, Blanks, and Uncertainty Calculations: Typically, each cartridge was counted 2-6 times using different counters. Results were averaged and the standard deviation of the mean (sdom) was calculated. The uncertainty was also calculated from the uncertainties of each measurement. These were usually quite close to the sdom, and the larger of the two counting uncertainties was assumed. Contributions of uncertainties from crosstalk corrections and the uncertainty from cartridge efficiency were included by error propagation expressions. Total Ac and its uncertainty were divided by the water volume pumped to find concentration. Blanks were negligible, based on measuring unused cartridges or those deployed in pumps that did not pump.

Excess 227Ac: Analyses of the 227Ac parent 231Pa were done on Niskin water samples that were usually a few meters vertically from the pumps. These were performed by collaborating groups (C. Hayes of U. So. Miss., R. Anderson of LDEO and L. Edwards of U. Minnesota). Their results were subtracted from total Ac to calculate excess 227Ac. In a few cases, it was necessary to interpolate over larger distances, but the uncertainty from this is expected to be small. No effect on Ac uncertainties is expected, as the 231Pa measurements have a precision of only a few percent. Most samples that were not near the bottom have negligible excess 227Ac in comparison to the uncertainties, indicating the 227Ac is accurately calibrated. This is illustrated in Fig. 5, as a plot of total dissolved 227Ac vs. total 231Pa for samples from the upper 2 km, where paired cartridges were deployed.

Quality Flags: Quality flags have been assigned to data based on the following descriptions:

0 = no quality control.
1 = good value; A & B cartridges deployed.
2 = probably good; only A cartridge deployed; larger uncertainty; total Ac less than zero but within uncertainty of zero; adjusted to zero.
3 = probably bad; inconsistent with other data.
4 = bad value.
5 = changed value.
6 = below detection; total Ac less than zero; adjust to zero.
7 = value in excess of detection.
8 = interpolated value.
9 = missing value; insufficient pump volume, pump failure, or no cartridge delivered.

BCO-DMO Processing Description

- Imported original file "RR1815_dataTemplate_227Ac.xls" into the BCO-DMO system.
- Renamed fields to comply with BCO-DMO naming conventions.
- Created date-time fields in ISO 8601 format.
- Removed empty fields: End_Latitude, End_Longitude, Rosette_Position.
- Saved the final file as "941157_v1_gp15_dissolved_227ac_leg2.csv".

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Parameters

Parameter	Description	Units
Station_ID	Station number	unitless
Event_ID	Event number	unitless
Gear_ID	Sampling instrument	unitless
Start_ISO_DateTime_UTC	Date and time (UTC) at start of sampling in ISO 8601 format	unitless
Start_Date_UTC	Date (UTC) at start of sampling	unitless

Start_Time_UTC	Time (UTC) at start of sampling	unitless
End_ISO_DateTime_UTC	Date and time (UTC) at end of sampling in ISO 8601 format	unitless
End_Date_UTC	Date (UTC) at end of sampling	unitless
End_Time_UTC	Time (UTC) at end of sampling	unitless
Start_Latitude	Latitude at start of sampling	decimal degrees North
Start_Longitude	Longitude at start of sampling	decimal degrees East
Sample_ID	GEOTRACES sample ID number	unitless
Sample_Depth	Sample depth	meters (m)
Ac_227_D_CONC_PUMP_rxwrrl	Concentration (or activity) of dissolved 227Ac in uBq/kg	micro becquerel per kilogram (uBq/kg)
SD1_Ac_227_D_CONC_PUMP_rxwrrl	One standard deviation of Ac_227_D_CONC_PUMP_rxwrrl	micro becquerel per kilogram (uBq/kg)
Flag_Ac_227_D_CONC_PUMP_rxwrrl	Quality flag for Ac_227_D_CONC_PUMP_rxwrrl	unitless
DAB	Distance above bottom	meters (m)
Pa231_uBq_kg	Concentration (or activity) of dissolved Pa231 in uBq/kg	micro becquerel per kilogram (uBq/kg)
Excess_227Ac_D_uBq_kg	Excess 227Ac in uBq/kg	micro becquerel per kilogram (uBq/kg)
sig1_Excess_227Ac_D_uBq_kg	[need definition]	micro becquerel per kilogram (uBq/kg)
Ac227_D_dpm_m3	Concentration (or activity) of dissolved 227Ac in dpm/m3	disintegrations per minute per cubic meter (dpm/m3)
sig1_227Ac_D_dpm_m3	[need definition]	disintegrations per minute per cubic meter (dpm/m3)
Pa231_dpm_m3	Concentration (or activity) of dissolved Pa231 in dpm/m3	disintegrations per minute per cubic meter (dpm/m3)

Excess_227Ac_D_dpm_m3	Excess 227Ac in dpm/m3	disintegrations per minute per cubic meter (dpm/m3)
sig1_227Ac_dpm_m3	[need definition]	disintegrations per minute per cubic meter (dpm/m3)
Cartridges	Identifies which cartridge(s) were used	unitless

Instruments

Dataset-specific Instrument Name	McLane Pumps
Generic Instrument Name	McLane Pump
Generic Instrument Description	McLane pumps sample large volumes of seawater at depth. They are attached to a wire and lowered to different depths in the ocean. As the water is pumped through the filter, particles suspended in the ocean are collected on the filters. The pumps are then retrieved and the contents of the filters are analyzed in a lab.

Dataset-specific Instrument Name	RaDeCC system made by Scientific Computing, Inc.
Generic Instrument Name	Radium Delayed Coincidence Counter
Generic Instrument Description	The RaDeCC is an alpha scintillation counter that distinguishes decay events of short-lived radium daughter products based on their contrasting half-lives. This system was pioneered by Giffin et al. (1963) and adapted for radium measurements by Moore and Arnold (1996). References: Giffin, C., A. Kaufman, W.S. Broecker (1963). Delayed coincidence counter for the assay of actinon and thoron. J. Geophys. Res., 68, pp. 1749-1757. Moore, W.S., R. Arnold (1996). Measurement of 223Ra and 224Ra in coastal waters using a delayed coincidence counter. J. Geophys. Res., 101 (1996), pp. 1321-1329. Charette, Matthew A.; Dulaiova, Henrieta; Gonneea, Meagan E.; Henderson, Paul B.; Moore, Willard S.; Scholten, Jan C.; Pham, M. K. (2012). GEOTRACES radium isotopes interlaboratory comparison experiment. Limnology and Oceanography - Methods, vol 10, pg 451.

Deployments

RR1815

Website	https://www.bco-dmo.org/deployment/776917
Platform	R/V Roger Revelle
Report	https://datadocs.bco-dmo.org/docs/geotraces/GEOTRACES_PMT/casciotti/data_docs/GP15_Cruise_Report_with_ODF_Report.pdf
Start Date	2018-10-24
End Date	2018-11-24
Description	Additional cruise information is available from the Rolling Deck to Repository (R2R): https://www.rvdata.us/search/cruise/RR1815

Project Information

US GEOTRACES Pacific Meridional Transect (GP15) (U.S. GEOTRACES PMT)

Website: http://www.geotraces.org/

Coverage: Pacific Meridional Transect along 152W (GP15)

A 60-day research cruise took place in 2018 along a transect form Alaska to Tahiti at 152° W. A description of the project titled "*Collaborative Research: Management and implementation of the US GEOTRACES Pacific Meridional Transect*", funded by NSF, is below. Further project information is available on the US GEOTRACES website and on the cruise blog. A detailed cruise report is also available as a PDF.

Description from NSF award abstract:
GEOTRACES is a global effort in the field of Chemical Oceanography in which the United States plays a major role. The goal of the GEOTRACES program is to understand the distributions of many elements and their isotopes in the ocean. Until quite recently, these elements could not be measured at a global scale. Understanding the distributions of these elements and isotopes will increase the understanding of processes that shape their distributions and also the processes that depend on these elements. For example, many "trace elements" (elements that are present in very low amounts) are also important for life, and their presence or absence can play a vital role in the population of marine ecosystems. This project will launch the next major U.S. GEOTRACES expedition in the Pacific Ocean between Alaska and Tahiti. The award made here would support all of the major infrastructure for this expedition, including the research vessel, the sampling equipment, and some of the core oceanographic measurements. This project will also support the personnel needed to lead the expedition and collect the samples.

This project would support the essential sampling operations and infrastructure for the U.S. GEOTRACES Pacific Meridional Transect along 152° W to support a large variety of individual science projects on trace element and isotope (TEI) biogeochemistry that will follow. Thus, the major objectives of this management proposal are: (1) plan and coordinate a 60 day research cruise in 2018; (2) obtain representative samples for a wide variety of TEIs using a conventional CTD/rosette, GEOTRACES Trace Element Sampling Systems, and in situ pumps; (3) acquire conventional CTD hydrographic data along with discrete samples for salinity, dissolved oxygen, algal pigments, and dissolved nutrients at micro- and nanomolar levels; (4) ensure that proper QA/QC protocols are followed and reported, as well as fulfilling all GEOTRACES intercalibration protocols; (5) prepare and deliver all hydrographic data to the GEOTRACES Data Assembly Centre (via the US BCO-DMO data center); and (6) coordinate all cruise communications between investigators, including preparation of a hydrographic report/publication. This project would also provide baseline measurements of TEIs in the Clarion-Clipperton fracture zone (~7.5°N-17°N, ~155°W-115°W) where large-scale deep sea mining is planned. Environmental impact assessments are underway in partnership with the mining industry, but the effect of mining activities on TEIs in the water column is one that could be uniquely assessed by the GEOTRACES community. In support of efforts to communicate the science to a wide audience the investigators will recruit an early career freelance science journalist with interests in marine science and oceanography to participate on the cruise and do public outreach, photography and/or videography, and social media from the ship, as well as to submit articles about the research to national media. The project would also support several graduate students.

U.S. GEOTRACES Pacific Meridional Transect: Measurements of Actinium-227 to Trace Solute Transport (PMT Actinium-227)

NSF Award Abstract:
The goal of the international GEOTRACES program is to understand the distributions of trace chemical elements and their isotopes in the oceans. This project will support the measurement of the naturally occurring radioisotope actinium-227 (Ac-227) in water samples from the 2018 U.S. GEOTRACES expedition in the Pacific Ocean, running south from Alaska to Tahiti. In addition, the investigators plan to analyze lead-210 and actinium-227 in sediment cores collected by the project, in order to constrain the source of Ac-227 to the water from bottom sediments. The value of measuring Ac-227 in the water column, particularly if the bottom source function is known, lies in the potential to use it to measure rates of mixing and transport of the water. These transport estimates can then be applied to understand the distributions of other trace elements measured on the expedition. The project would support a graduate student, several undergraduates, and a high school student, as well as outreach to local veterans groups encouraging their participation in STEM programs.

Despite having a half-life (22 years) that is well suited for the study of both vertical and lateral transport in the deep ocean, few Ac-227 measurements have been made in the deep sea. Recent advances in instrumentation facilitate this analysis, and the synergy provided by the GEOTRACES program will provide an ideal opportunity to obtain additional data. In addition, Ac-227 will be of value in defining the spatial variability of mixing rates across a broad reach of the central Pacific, particularly when combined with estimates based on Ra-228 (6 year half-life) distribution, a tracer field that a collaborating GEOTRACES program will determine. By using multiple tracers with different half-lives, influences of mixing and advection may be distinguished, allowing a more complete understanding of the deep Pacific dynamics. These transport estimates can then be applied to concentration fields of other solutes, including metals and nutrients, but will be of particular importance for alkalinity and silicic acid, which should have strong benthic sources.

This award reflects NSF's statutory mission and has been deemed worthy of support through evaluation using the Foundation's intellectual merit and broader impacts review criteria.

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Program Information

U.S. GEOTRACES (U.S. GEOTRACES)

Website: http://www.geotraces.org/

Coverage: Global

GEOTRACES is a SCOR sponsored program; and funding for program infrastructure development is provided by the U.S. National Science Foundation.

GEOTRACES gained momentum following a special symposium, S02: Biogeochemical cycling of trace elements and isotopes in the ocean and applications to constrain contemporary marine processes (GEOSECS II), at a 2003 Goldschmidt meeting convened in Japan. The GEOSECS II acronym referred to the Geochemical Ocean Section Studies To determine full water column distributions of selected trace elements and isotopes, including their concentration, chemical speciation, and physical form, along a sufficient number of sections in each ocean basin to establish the principal relationships between these distributions and with more traditional hydrographic parameters;

* To evaluate the sources, sinks, and internal cycling of these species and thereby characterize more completely the physical, chemical and biological processes regulating their distributions, and the sensitivity of these processes to global change; and

* To understand the processes that control the concentrations of geochemical species used for proxies of the past environment, both in the water column and in the substrates that reflect the water column.

GEOTRACES will be global in scope, consisting of ocean sections complemented by regional process studies. Sections and process studies will combine fieldwork, laboratory experiments and modelling. Beyond realizing the scientific objectives identified above, a natural outcome of this work will be to build a community of marine scientists who understand the processes regulating trace element cycles sufficiently well to exploit this knowledge reliably in future interdisciplinary studies.

Expand "Projects" below for information about and data resulting from individual US GEOTRACES research projects.

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Funding

Funding Source	Award
NSF Division of Ocean Sciences (NSF OCE)	OCE-1830168

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