Biogeochemical Studies of the South Pacific Ocean Using Thorium and Protactinium Isotopes

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Submitted in partial fulfillment of the requirements for the degree of Doctor of Philosophy in the Graduate School of Arts and Sciences

COLUMBIA UNIVERSITY

2020
ABSTRACT

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The ocean is both a repository and reactor for chemicals at the Earth’s surface. As chemicals enter the ocean they are taken up by organisms, transported by currents, reacted with particle surfaces, and eventually buried at the seafloor. This dynamic set of chemical processes and exchanges are encapsulated by the term biogeochemistry.

Marine biogeochemistry can be broadly deconstructed into two parts: ocean interfaces and internal cycling. Ocean interfaces are where chemical constituents enter and leave the ocean, including the air-sea boundary, mid-ocean ridges, continental margins, and rivers. Internal cycling is how chemical constituents are reacted, transported, taken up by organisms, and redistributed within the ocean. For a complete understanding of marine biogeochemical cycles, the input, output, and internal cycling rates of major and trace elements must be quantified. However, this rate information is difficult to infer from the observational snapshots of chemical concentrations typically collected on oceanographic expeditions.

The long-lived radioisotopes of thorium (Th) and protactinium (Pa) provide an opportunity to quantify these elusive biogeochemical rates. The radiogenic isotopes $^{230}$Th and $^{231}$Pa are produced at a uniform rate throughout the water column by uranium decay. A third isotope, $^{232}$Th, is primordial and brought to the ocean by the dissolution of lithogenic matter. While uranium is highly soluble, Th and Pa are highly insoluble, and are rapidly
removed from solution by adsorption onto settling particle matter. Due to their insolubility and known input rates, $^{230}$Th and $^{231}$Pa have well-constrained 1-d mass budgets between radiogenic production and scavenging removal.

This thesis explores new ways Th and Pa isotopes can be used to understand and quantify rates of biogeochemical processes in the South Pacific Ocean, and to assess how measurements of sedimentary Th and Pa isotopes can be used to study these processes in the geologic past. In chapter 1, I characterize the effects of submarine hydrothermal activity on the distributions of $^{230}$Th and $^{231}$Pa, finding strong removal due to adsorption by Fe and Mn oxide particles. In chapter 2, I utilize the radioactive disequilibria of two additional radiogenic thorium isotopes with much shorter half-lives, $^{234}$Th and $^{228}$Th, to constrain the kinetics of Th scavenging by hydrothermal particles.

Chapter 3 switches gears towards quantifying the internal cycling of particulate organic carbon in the subtropical South Pacific. Using a new method based on measurements of particulate $^{230}$Th, I generated high-resolution water column profiles of particulate organic carbon flux to constrain carbon regeneration length scales in both oligotrophic and oxygen minimum zone settings. In chapter 4, I demonstrate the importance of isopycnal mixing in transporting $^{230}$Th, $^{231}$Pa, and $^{232}$Th into the Pacific Southern Ocean, showing the first high-resolution dissolved Th and Pa data from the region.

Chapter 5 provides estimates of dust input spanning the South Pacific using two methods based on paired $^{230}$Th-$^{232}$Th, evaluates the flux of dust-borne iron, and discusses the impacts on measured and modeled nitrogen fixation rates in the South Pacific gyre. Finally, in chapter 6 I present enigmatic profiles of Th and Pa isotopes from the semi-enclosed Peru and Bauer Basins, with anomalous Th and Pa removal extending 1-2km above the
seafloor. I hypothesize that these depletions are related to the extent of water mass contact with the seafloor, allowing for scavenging removal of Th and Pa by resuspended sediments.
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Acknowledgements

My time at Lamont has been made magical by the mentors, peers, colleagues, collaborators, and friends I’ve met here. My first thanks, though, go to my family – to my parents, for always supporting me and keeping me inspired, interested, and passionate about my work, and my sister Risa, who embarked on her Ph.D. journey at the same time, and has kept me grounded and motivated – especially when it comes to getting rid of rocks!

I am in awe of my advisor Bob Anderson, and his dedication not only to science but to fellow scientists. Thank you Bob, for motivating me to seek the deepest truths possible, for pushing me to be the best scientist I can be, and for providing me the freedom to pursue a huge array of topics and ideas, whether they fit within the framework of my thesis work or not. My committee: Gisela Winckler, Ryan Abernathey, Andreas Thurnherr, and Tom Weber, has provided fantastic feedback on the work in this thesis. Gisela, thank you also for being such a fantastic mentor and role model for me as a scientist and as a person – and for guiding me through the most difficult times of my Ph.D.

The work in this thesis would not have been possible without the incredible dedication and guidance of Marty Fleisher. Marty has patiently taught me all I know about analytical chemistry, mass spectrometry, and instrumental music. I am eternally grateful to him, and happy to count him as a colleague and friend.
I have learned immensely from working with many other members of the Lamont community. Dorothy Peteet, Jon Nichols, and Linda Heusser gave me my start at Lamont, teaching me the fundamentals of doing good science, and the importance of doing fun science. Steve Goldstein, Sid Hemming, Nick Christie-Blick, Mo Raymo, and Billy D’Andrea gave me immensely valuable geologic field experiences. I learned immensely working as a teaching assistant for Joerg Schaefer, Wally Broecker, and Terry Plank. I am also deeply grateful to Terry for encouraging me to think beyond the ocean, and for many years of both academic and intellectual guidance.

One of the best parts about working at Lamont has been the amazing collection of young scientists working alongside me. The student and postdoc communities here are incredibly smart, fun, and forward-looking. I’m eternally thankful for the friends I’ve made here, including (but not limited to): Laura Haynes, Lorelei Curtin, Logan Brenner, Sam Phelps, Maayan Yehudai, Bridgit Boulahanis. The PITHe working group – my de facto extended lab group, has been an amazing part of the last couple years at Lamont, and one of the most intellectually-stimulating parts of my Lamont experience. Thanks to all the PITHeans who made it so great: Gisela, Bob, Marty, Jerry McManus, Kassandra Costa, Allison Jacobel, Jennifer Middleton, Paulina Pinedo, Julia Gottschalk, Erin Black, Lauren Kipp, Jordan Abell, Sophie Hines, and Yuxin Zhou. Kassandra Costa and Jenny Middleton in particular – thank you for helping make PITHe a reality – and for being such amazing friends, colleagues, collaborators, and co-conspirators.

It would not have been possible to complete this Ph.D. without a great cohort of friends who have made living in New York City an absolute delight. To the Riverbank tennis crew – Jonathan, Thomas, and Nicolas – what a treat it’s been to have a well-matched doubles
squad. Nicolas, thank you for providing an unexpected outlet for my second passion – obscure sports information. John Isner is not elite. To Jason Bell and Alan Seltzer – thank you for being so passionate about what you both do, and for providing avenues to do exciting research far beyond the scope of my thesis work - you guys are the best. To Ben and Alec, my childhood friends now in NYC, and their partners Hannah and Betsy – what fun it’s been to hang out all these years. Thanks for believing protactinium is a real element – remember that its oceanography, not oceanology. Finally, to Taylor, Rick, Katherine, and Sarah – the squuuuaaaad. I wouldn’t have made it through this Ph.D. without you all. Thanks for making sure I never forget what life is all about.
To Casey Ichniowski, who taught me that it’s not just about sports.
Chapter 1

*Intense Hydrothermal Scavenging of* $^{230}$Th and $^{231}$Pa in the Deep Southeast Pacific.*

Note: This chapter was published in the journal *Marine Chemistry* in 2018.

Abstract

Hydrothermal circulation and subsequent eruption of seawater at mid-ocean ridges and back-arc basins has great potential to modulate deep ocean biogeochemistry, acting as both a source and a sink for many trace elements and their isotopes. The influence of hydrothermal vents as a source of iron and manganese has been demonstrated in all ocean basins. However, the long-range impact of scavenging by hydrothermal particles has yet to be documented in detail. We use dissolved and particulate measurements of long-lived radiogenic ($^{230}$Th, $^{231}$Pa) and primordial ($^{232}$Th) radionuclides to investigate the nature and geographic scale of scavenging processes occurring within a hydrothermal plume in the Southeast Pacific Ocean sampled during the GEOTRACES GP16 section. Due to their radioactive disequilibrium with respect to production by their parent uranium isotopes,

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230Th and 231Pa provide unique insights into the rates of scavenging. We find strong deficits in 230Th and 231Pa coincident with elevated particulate Mn and Fe(OH)₃, indicating that trace metal scavenging is widespread and likely the result of the strong affinity of trace metals for nanoparticulate metal surface sites. The chemical composition of the particulate material is closely linked to the scavenging intensity of 230Th and 231Pa, expressed as distribution coefficients between solid and solution. A comparison of 230Th and 231Pa inventories with mantle-derived 3He as well as a mass balance of 230Th and 231Pa suggests continuous scavenging removal over the course of the entire 4000 km transect. Unlike the two radiogenic isotopes, 232Th is enriched above what would be expected from assuming identical scavenging behavior to 230Th, indicating a hydrothermal source of colloidal, unreactive 232Th.

1.1 Introduction

Throughout the global mid-ocean ridge system, hydrothermal circulation occurs when cold seawater percolates through and reacts with the upper ocean crust, heating to temperatures surpassing 400°C. After reacting with the host rock, the hot, geochemically-altered fluids are sufficiently buoyant to rise back towards the ocean floor, where they are re-emitted into the deep ocean via submarine vents. The fluid rapidly mixes with ambient seawater and rises to form a neutrally buoyant hydrothermal plume (German and Seyfried 2014). Due to high particle abundance (e.g. Estapa et al. 2015; Feely et al. 1987) and unique chemical and isotopic composition with respect to ambient deep ocean waters (German and Seyfried 2014), hydrothermal activity has great potential for modulating el-
elemental budgets and ocean chemistry. Studies have identified hydrothermal plumes as a large source of many elements, such as iron and manganese (Klinkhammer et al. 1977; Resing et al. 2015; Saito et al. 2013), zinc (Roshan et al. 2016; Von Damm et al. 1985), and a large sink for many others, including rare earth elements (German et al. 1990), uranium (Michard and Albarède 1985), and thorium (German et al. 1991, 2002; Kadko 1996), via adsorption onto or co-precipitation with hydrothermal particles.

Whether hydrothermal plumes exert basin-scale influence on geochemical budgets in the ocean has been a much-debated topic. Hydrothermal inputs of iron have received significant attention (Tagliabue and Resing 2016; Tagliabue et al. 2010, 2014) due to the biological necessity of Fe and the broad regions of the surface ocean in which primary production is limited by a lack of iron (e.g. Falkowski et al. 1998). Early studies argued that, despite iron being heavily enriched ($10^6$ times greater than seawater) in hydrothermal vent fluids, the long-range effect of hydrothermal activity on dissolved iron content in the deep ocean would be limited by rapid precipitation of oxides and sulfides when vent fluids initially came into contact with oxygenated seawater (Feely et al. 1996; German et al. 1991; Rudnicki and Elderfield 1993). However, in recent years the paradigm of negligible far-field transport of hydrothermal iron has been upended by several studies finding plumes of dissolved iron and manganese thousands of kilometers away from their sources along the global mid-ocean ridge system, indicating that stabilization and/or slow oxidation rates in hydrothermal environments allow Fe to spread throughout entire ocean basins (Bennett et al. 2008; Fitzsimmons et al. 2014; Resing et al. 2015; Saito et al. 2013; Sander and Koschinsky 2011). The long-range spread of hydrothermal plume particles and their influence on trace metal scavenging remain mysteries.
Two unique tracers of particulate scavenging are the long-lived radionuclides of protactinium ($^{231}$Pa) and thorium ($^{230}$Th), as their disequilibria from production by parent nuclides ($^{235}$U and $^{234}$U, respectively) provide rare ‘clocks’ for calculating removal rates with respect to adsorption onto particles. Dissolved uranium is conservative in the ocean and the distribution of uranium isotopes is well-mixed (Andersen et al. 2010), so the production rates of $^{231}$Pa and $^{230}$Th are well-known, and nearly constant throughout the ocean. Scavenging residence times for $^{231}$Pa (50-200 years) and $^{230}$Th (10-40 years) (Henderson and Anderson 2003) are much shorter than their respective half-lives of 32,760 years (Robert et al. 1969) and 75,584 years (Cheng et al. 2013) so their removal from the water column can be treated as being quantitatively equal to their known production rates. Water column variations in the activities of $^{231}$Pa and $^{230}$Th are the result of factors related to their removal, redistribution, or partitioning between phases – factors such as particle flux, particle composition, advection, and diffusion.

Much like iron, early studies on the scavenging of $^{230}$Th and $^{231}$Pa in hydrothermal plumes were focused on sites nearby ridge crest sources. Ridge flank sediments showed enhanced removal of $^{230}$Th and $^{231}$Pa associated with downcore peaks in Fe and Mn content, reflecting hydrothermal scavenging (German et al. 1993, 1997; Shimmield and Price 1988). However, peaks in $^{230}$Th and $^{231}$Pa activity were not always associated with hydrothermal metal anomalies in these cores.

Other studies focused on the signature of hydrothermal scavenging in the water column. German et al. (1991) found a positive, linear correlation between total (dissolved plus particulate) $^{230}$Th and particulate Fe in samples within two kilometers of an active vent site at the TAG hydrothermal vent field. This is slightly unexpected, given that high
concentrations of sinking particles would be expected to generate a deficit of \(^{230}\)Th. The authors argued that the elevated total \(^{230}\)Th was the result of re-entrainment of particles that had previously sunken out of the hydrothermal plume.

German et al. (2002) measured particulate \(^{230}\)Th in sediment trap samples from within 20 m of an active hydrothermal vent site at 13\(^\circ\)N on the East Pacific Rise, and found \(^{230}\)Th fluxes three times greater than in the overlying water column. This was explained by adsorption of dissolved \(^{230}\)Th onto particles setting up a strong dissolved \(^{230}\)Th gradient away from vent activity, with the resulting diffusive transport causing \(^{230}\)Th on sinking particles to be greater than what was produced in overlying waters. The spatial extent of this lateral diffusive input flux is not well understood. Only recently have mid-depth \(^{230}\)Th deficits at sites thousands of kilometers away from ridge systems been attributed to hydrothermal scavenging. Lopez et al. (2015) found a depletion in dissolved and total \(^{230}\)Th in 2500 m depth waters in the Central Equatorial Pacific, 5000 km downstream of the East Pacific Rise (EPR). These authors attributed their signal to depletion of \(^{230}\)Th from the water column by near-axis hydrothermal scavenging, and subsequent advection of the depletion signal westward towards their site.

Here we present dissolved and particulate \(^{230}\)Th, \(^{231}\)Pa, and \(^{232}\)Th data from a hydrothermal plume in the South Pacific Ocean extending over 4000km away from the EPR. We use the radioactive disequilibrium of these nuclides in the dissolved phase and enrichment in the particulate phase to understand the particle dynamics and scavenging behavior of trace metals in regions of intense hydrothermal activity.
1.2 Materials and Methods

1.2.1 Cruise setting and Sampling Locations

GEOTRACES cruise GP16 took place between Manta, Ecuador and Papeete, Tahiti aboard the RV Thomas G. Thompson between 25 October and 20 December 2013 (Figure 1.1). Sampling for dissolved and particulate protactinium and thorium isotopes took place at 20 stations, 10 of which are downstream of the South East Pacific Rise (SEPR) ridge axis, and one of which (Station 18) lies directly above the ridge axis. The SEPR is one of the fastest-spreading ridge systems in the world, with a spreading rate of roughly 14.5 cm yr\(^{-1}\) (Feely et al. 1996). Hydrothermal activity along the SEPR is well-documented by anomalously high mantle-derived \(\textsuperscript{3}\text{He}\) (\(\textsuperscript{3}\text{He}_{xs}\)) downstream of the ridge axis throughout the Pacific Basin (Lupton and Craig 1981), as well as the areal extent of metalliferous sediments surrounding the ridge system (Boström et al. 1969). Along 11–15ºS, independent lines of evidence point towards topographically-steered westward flow between 2000 and 3000 m depth above the ridge axis (Faure and Speer 2012; Hautala and Riser 1993; Reid 1986), placing the GP16 stations west of the SEPR downstream of the hydrothermal ac-
ivity along the ridge axis.

1.2.2 Sample Collection and Analysis

Radionuclide samples were collected according to standard GEOTRACES protocols (Anderson et al. 2012), then analyzed by two intercalibrated labs: Lamont-Doherty Earth Observatory of Columbia University (LDEO) and University of Minnesota (UMN). For dissolved samples, 4–5 l of seawater were filtered through a 0.45 μm Acropak capsule filter at sea and acidified to pH = 2 using 6M hydrochloric acid. Particulate samples were collected with McLane Research Laboratories in-situ pumps, using a 51 μm polyester screen to collect particles >51 μm, followed by two stacked 0.8 μm filters to collect small particles (0.8–51 μm). Details of the sampling methodology for collecting particulate samples for radionuclide analysis can be found in Hayes et al. (2015a). The full procedure describing analysis of particulate samples for composition can be found in Lam et al. (2018). Briefly, biogenic opal was determined by spectrophotometry, particulate organic carbon in the small size fraction was determined by flash combustion, and particulate inorganic carbon was measured by coulometry. The mass of lithogenic materials was determined by measuring aluminum via digestion and subsequent analysis by inductively-coupled plasma mass spectrometry (ICP-MS). Particulate aluminum concentrations were then divided by the Al content of upper continental crust (UCC) to determine the mass of particulate lithogenic material. Particulate concentrations of Fe oxyhydroxides and Mn oxides were determined as excess Fe and Mn over their lithogenic contributions, by subtracting lithogenic Fe and Mn from bulk Fe and Mn concentrations (measured by ICP-MS) using
Figure 1.2: Sections of dissolved $^{230}\text{Th}$ and $^{231}\text{Pa}$ activities on GP16. Station numbers for which results are presented here are indicated across the top of each station.

Al concentrations and Fe/Al and Mn/Al ratios in UCC, and assumed to have the compositions Fe(OH)$_3$ and MnO$_2$. Total suspended particulate mass (SPM) was determined by summing the individual particulate components: Particulate organic matter, opal, calcium carbonate, lithogenics, Fe oxyhydroxides, and Mn oxides.

The analysis procedures for $^{230}\text{Th}$ and $^{231}\text{Pa}$ are as follows. All samples were stored and analyzed on-shore. Dissolved samples were spiked with $^{229}\text{Th}$ and $^{233}\text{Pa}$, co-precipitated with Fe oxyhydroxide, preconcentrated, and digested with HNO$_3$, HF, and HClO$_4$. Filter
samples were completely dissolved using HNO$_3$ and HClO$_4$ before iron co-precipitation (Hayes et al. 2015a). Both dissolved and particulate thorium and protactinium isotopes were then isolated using anion exchange chromatography and analyzed using ICP-MS. Full details of the LDEO and UMN analytical procedures are documented in Anderson et al. (2012) and Shen et al. (2003; 2002, 2012). Dissolved samples are corrected for ingrowth of $^{230}$Th and $^{231}$Pa by uranium decay during sample storage. We then apply two separate corrections. When evaluating the effects of scavenging on radionuclides in the water column, we correct both dissolved and particulate $^{230}$Th and $^{231}$Pa for lithogenic contributions, as outlined by Hayes et al. (2013a). Data corrected in this manner typically have the subscript xs. With the exception of calculating distribution coefficients (K$_d$), all measurements and discussions of $^{230}$Th and $^{231}$Pa are corrected for ingrowth during sample storage and lithogenic contributions. Following Hayes et al. (2015b), the particulate pool of $^{230}$Th and $^{231}$Pa used for determining K$_d$ values is the sum of the xs particulate concentration and the adsorbed component of the lithogenic contribution. We denote $^{230}$Th$_{pads}$ as the combination of these two pools. GEOTRACES GP16 data are archived at the Biological and Chemical Oceanography Data Management Office (BCO-DMO), and are included in the 2017 GEOTRACES Intermediate Data Product (Schlitzer et al. 2018).

1.2.3 Blanks and Uncertainties

Procedural blanks for dissolved samples were determined by processing 5 l of Milli-Q water in acid-cleaned cubitainers, acidified to pH = 2 using 6 M HCl. Average procedural blanks for dissolved samples were 7 pg $^{232}$Th, 0.4 fg $^{230}$Th, and 0.1 fg $^{231}$Pa. For particulate
samples, blanks were measured using “dipped blanks” – acid-cleaned filters deployed on each pump cast, but with no seawater pumped over them (Lam et al. 2018). The pooled average of all dipped blanks were used for background correction, and were 21.52 pg $^{232}$Th, 1.17 fg $^{230}$Th, and 0.07 fg $^{231}$Pa.

For thorium, measurement uncertainties include propagated errors from ICP-MS isotope ratio measurements, spike concentrations, and blank corrections. For protactinium, uncertainties included the same factors as for thorium, but also instrumental mass bias, yield correction, and machine blank. In addition to analytical precision, we also assessed the long-term reproducibility of our measurements by measuring aliquots of two standard solutions containing $^{232}$Th, $^{230}$Th, and $^{231}$Pa: SW STD 2010-1 (Anderson et al. 2012) and SW STD 2015-1. Standard measurements during analysis of dissolved samples gave reproducibility of 1.44% for $^{230}$Th, 2.14% for $^{232}$Th, and 3.89% for $^{231}$Pa. During analysis of particulate samples, reproducibility was 1.03% for $^{230}$Th, 1.12% for $^{232}$Th, and 2.95% for $^{231}$Pa.

1.3 Results and Discussion

1.3.1 Hydrothermal Scavenging of $^{230}$Th, and $^{231}$Pa

In this paper, we primarily focus on data from below 1000 m depth from the stations west of the EPR along GP16. The multitude of other features affecting $^{230}$Th and $^{231}$Pa along the eastern portion of the section and in the upper 1000 m will be the subjects of future work. In the upper 2000 m, dissolved and particulate $^{230}$Th, and $^{231}$Pa display the linear
increase with depth predicted by reversible scavenging (Bacon and Anderson 1982). At stations west of the EPR, strong depletions in $^{230}$Th, and $^{231}$Pa are present below 2000 m (Figure 1.2), coincident with the depths of hydrothermal enrichment of dissolved $^3$He$_{xs}$ (Jenkins et al. 2018), Fe, Mn, Al (Resing et al. 2015) and Zn (Roshan et al. 2016) along the same section. The depth of the minima in dissolved $^{230}$Th and $^{231}$Pa varies by <100 m across the section, between 2500 and 2600 m, below which $^{230}$Th and $^{231}$Pa increase towards the bottom (Figure 1.3). Conversely, particulate $^{230}$Th and $^{231}$Pa are enriched below 2000 m, with maxima at similar depths as the dissolved minima, before decreasing towards the seafloor (Figure 1.3). This hydrothermal scavenging signal persists at all sampling locations west of the ridge axis (stations 18-36), over 4000 km away from the vent sites.
Reversible scavenging predicts that 1-dimensional profiles of dissolved, particulate, and total \(^{230}\text{Th}\) and \(^{231}\text{Pa}\) will increase linearly with depth (Bacon and Anderson 1982). Deviations from reversible scavenging at depth must therefore reflect some combination of local anomalous scavenging behavior and lateral dispersal (Hayes et al. 2015a). The reversible scavenging model provides a baseline against which hydrothermal scavenging can be quantified. As previously suggested (Deng et al. 2014; Hayes et al. 2015a) and performed (Lopez et al. 2015), we quantify the degree of hydrothermal scavenging as a
percent depletion of total $^{230}$Th and $^{231}$Pa relative to the expected concentration at depth due to reversible scavenging (Figure 1.4a).

We first predict reversible scavenging profiles of total $^{230}$Th and $^{231}$Pa based on a regression of concentration and depth between 300 and 1500 m. The depth ranges were chosen to avoid changes in slope present in the uppermost water column (Hayes et al. 2015c) and hydrothermal influence at depth. We extrapolate the derived regressions to depths below 1500 m to calculate the values of total $^{230}$Th and $^{231}$Pa concentration predicted by reversible scavenging if no hydrothermal plume were present. Concentrations in this 300–1500 m depth range are nearly the same everywhere (Figure 1.3) so we compute only one reversible scavenging prediction each for $^{230}$Th and $^{231}$Pa. The observed concentration-depth relationships have correlation coefficients of $R^2=0.98$ for $^{230}$Th and $R^2=0.96$ for $^{231}$Pa. Following Resing et al. (2015), we designate the depth range of the hydrothermal plume as being between 2200 and 2800 m. For stations at which those exact depths were not sampled, we linearly interpolate $^{230}$Th and $^{231}$Pa onto those depths to facilitate integration within that range. Given the activity predicted by extrapolation of upper water column profiles ($A_{\text{predicted}}$) and the measured activity ($A_{\text{measured}}$) of total $^{230}$Th or $^{231}$Pa at each depth, we calculate percent depletion:

$$\text{Percent Depletion} = \frac{\int_{2200}^{2800} A_{\text{predicted}}(z) \, dz - \int_{2200}^{2800} A_{\text{measured}}(z) \, dz}{\int_{2200}^{2800} A_{\text{predicted}}(z) \, dz} \times 100$$  \hspace{1cm} (1.1)$$

While the terms in the equation are the same as in Lopez et al. (2015), note that we only integrate within the depth range of the hydrothermal plume, whereas Lopez et al. integrate over the full water column. We choose the narrower range to avoid potential
Figure 1.5: Percent depletion of A) total $^{230}\text{Th}_{xs}$ and B) total $^{231}\text{Pa}_{xs}$ plotted against the plume age, with Station 20 set at 0 age, using the distance of each station from station 20 divided by a constant plume spreading rate of 0.4 cm/s to estimate age. Points are derived for the 2200–2800 m depth interval at each station using Equation 1.1. Lines are linear regressions of percent removal with plume age.

influences of bottom water advection and nepheloid layer scavenging on our calculation. Consequently, it is possible that we underestimate the hydrothermal scavenging at some stations, especially those nearest to the ridge axis, where the scavenging signal might extend beyond the depth range of our integration window. Removal of $^{230}\text{Th}$ and $^{231}\text{Pa}$ is greatest at the ridge axis, both peaking near 70% depletion, before decreasing as waters move west away from the EPR (Figures 1.3a, 1.3b, and 1.5). By station 36, $^{230}\text{Th}$ only has 30% depletion, while $^{231}\text{Pa}$ maintains 55% depletion. To assess how geographically widespread the hydrothermal scavenging signature in $^{230}\text{Th}$ and $^{231}\text{Pa}$ might be, we compare percent depletion to the age of the plume waters since they left the EPR ridge axis – referred to as the plume age. Resing et al. (2015) found that station 18 had a low $^{3}\text{He}_{xs}$ inventory compared to stations further west of the ridge axis, suggesting that the far-field
hydrothermal plume is supplied by vents further south on the EPR, whereas station 18 is not. As a result, we use station 20, rather than station 18, as the initial point for deriving plume ages. For each station, we divide the distance to station 20 by a westward advection velocity of 0.4 cm/s (Hautala and Riser 1993) to determine the plume age. We perform a linear regression of percent depletion and plume age, with $R^2=0.79$ for $^{230}$Th and $R^2=0.89$ for $^{231}$Pa. By extrapolating the regressions to 0% depletion, we can determine the amount of time a hydrothermal scavenging signal will persist in the ocean for Th and Pa. We calculate depletion timescales (age of zero depletion) of 64 years for $^{230}$Th and 140 years for $^{231}$Pa. The depletion timescale of $^{230}$Th is long enough to validate the far-field findings of $^{230}$Th depletion seen along the Equator and near 8ºN by Lopez et al. (2015), as well as their supposition about hydrothermal scavenging being responsible for the mid-depth $^{230}$Th depletion seen in the eastern tropical North Pacific by Okubo et al. (2012). The zonal flows in the abyssal Pacific (e.g. Johnson and Talley 1997; Stommel 1982) allow for the persistence of the scavenging signal throughout the Pacific basin, whereas in the North Atlantic, along-segment flow (Thurnherr et al. 2002) may largely prevent the scavenging signal to be widespread beyond the confines of the axial valley of the Mid-Atlantic Ridge (MAR), although on the US GEOTRACES GA03 transect a small scavenging signal is also seen in the first station to the west of the MAR as well (Hayes et al. 2015a).
1.3.2 What process or phase is scavenging $^{230}$Th and $^{231}$Pa?

1.3.2.1 Distribution Coefficients and Fractionation Factors

The greater residence time of $^{231}$Pa compared to $^{230}$Th in the open ocean is explained by the lower reactivity with respect to adsorption onto particles of $^{231}$Pa (Anderson et al. 1983a). However, the two nuclides display different affinity for different particle types (Anderson et al. 1983b; Chase et al. 2002; Geibert and Usbeck 2004; Hayes et al. 2015b; Kretschmer et al. 2011). As a result, the relative removal rates of $^{231}$Pa and $^{230}$Th can vary with particle composition. Greater particle abundance will also affect the scavenging intensity of both $^{231}$Pa and $^{230}$Th. To determine the relative roles of particle composition and particle abundance on the scavenging of $^{231}$Pa and $^{230}$Th, we calculate the bulk partition coefficient ($K_d$) values, defined in units of activity per gram of particles divided by activity per gram of seawater:

$$K_d = \frac{A_{ads}^p}{A_{diss}} \times \frac{1}{SPM}$$  \hspace{1cm} (1.2)

The units of $A_{ads}^p$ and $A_{diss}$ are both activities per kg of seawater, while SPM has units of grams of particles per gram of seawater. In addition, we calculate the fractionation factor (Anderson et al. 1983a) defining the relative scavenging intensity of $^{230}$Th to $^{231}$Pa:

$$F\left(\frac{Th}{Pa}\right) = \frac{K_{Th}^d}{K_{Pa}^d}$$  \hspace{1cm} (1.3)

Particle concentration is thought to play an important role in modulating the scavenging intensity ($K_d$) of thorium and protactinium. $K_d$ values for $^{234}$Th (Honeyman et al. 1988b), compilations of both $^{234}$Th and $^{230}$Th (Hayes et al. 2015b; Henderson et al. 1999) and
$^{231}$Pa (Hayes et al. 2015b) have reciprocal relationships with particle mass, known as the "particle concentration effect". Why $K_d$ values decrease with increasing particle mass is not entirely understood. One possibility is that higher concentrations of thorium-binding colloids small enough to pass through typical filters keep the apparent $^{230}$Th concentration artificially high in the dissolved phase (Henderson et al. 1999). Another suggestion is that surface area per mass of particle decreases at greater particle mass, thereby reducing the number of available binding sites for scavenging metals (Henderson et al. 1999). Finally, recent inverse model estimates of thorium scavenging kinetics from the GA03 North Atlantic Zonal Transect cruise suggest that the rate at which thorium desorbs from particles appears to be positively correlated with particle concentration, which would also give rise to an apparent particle concentration effect (Lerner et al. 2017).

We compare the relationship between $K_d$ values for Th and Pa and SPM for the entire GP16 section with the relationship derived using exclusively the samples influenced by the hydrothermal plume, stations 18–30, from 2200 to 2800 m depth (Figure 1.6). Linear regressions for the non-plume samples of Log $K_d$ with Log SPM from the small size fraction (SSF) have the trends Log $K_d$(Th) [g/g] = 8.04-0.874*Log SPM [g/l] ($R^2$=0.72, p<0.001); Log $K_d$(Pa) [g/g] = 6.79-0.48*Log SPM [μg/l] ($R^2$=0.28, p<0.001). The samples from the plume form an array above the rest of the samples from the transect, indicating that whatever processes generate the negative correlation between $K_d$ and SPM are not responsible for the $K_d$ variations observed in the hydrothermal plume. In addition, the narrow range of SPM concentrations observed in the plume is too small for there to be a major particle concentration effect on $K_d$ values. The particle concentration effect only becomes apparent when $K_d$ is evaluated over particle concentrations spanning at least an
order of magnitude. The observed correlation between $K_d$ and SPM can be used to show the driving force behind the hydrothermal scavenging of $^{230}\text{Th}$ and $^{231}\text{Pa}$. We define $K$ as the ratio of particulate adsorbed to dissolved $^{230}\text{Th}$ or $^{231}\text{Pa}$. From Equation 1.2, it is apparent that $K$ can be calculated by multiplying $K_d$ with SPM. By calculating expected $K_d$ values for all samples using the statistical relationship between log $K_d$ and log SPM, along with the measured SPM concentration, we can then calculate an expected $K$ value for samples within the hydrothermal plume using the equation:

$$K^{\text{exp}} = K_d^{\text{exp}} \times \text{SPM}^{\text{meas}} \quad (1.4)$$
Figure 1.7: Measured and expected K values (particulate activity/dissolved activity) for A) $^{230}$Th and B) $^{231}$Pa at two stations from GP16. Expected K values determined by calculating expected K$_d$ values from the observed K$_d$-SPM relationships (Figure 1.6), and multiplying the expected K$_d$ values by the measured SPM concentration (Equation 1.4).

Here, K$^{exp}$ is the expected K value, K$_d^{exp}$ is the expected K$_d$ value calculated from the observed SPM concentration and the Log K$_d$-SPM regressions for Th and Pa, SPM$_{meas}$ is the measured SPM (Lam et al. 2018). The observed K values for both Th and Pa exceed the K values expected from the SPM concentration in the hydrothermal plume (Figure 1.7). These higher than expected K values and hydrothermal samples falling well above the K$_d$-SPM relationships (Figure 1.6) show that high particle concentration cannot be the primary mechanism responsible for the observed hydrothermal scavenging of $^{230}$Th and $^{231}$Pa on GP16.

The scavenging intensity of $^{230}$Th and $^{231}$Pa is also dictated in part by the composition of particles present in the water column. Early studies on the controls of scavenging intensity hypothesized that metal (particularly manganese) oxides play a critical role in
Table 1.1: Log $K_d$ values for $^{230}$Th and $^{231}$Pa and fractionation factors (F) for individual particle phases (Hayes et al. 2015b), EPZT background deep waters not influenced by hydrothermal activity (station 17, 2600m depth), EPZT hydrothermal plume (Station 18, 2550m depth), and the TAG hydrothermal plume (Hayes et al. 2015b).

<table>
<thead>
<tr>
<th>Phase</th>
<th>log $K_d$(Th)</th>
<th>log $K_d$(Pa)</th>
<th>F(Th/Pa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>POM</td>
<td>6.48</td>
<td>5.30</td>
<td>4.9</td>
</tr>
<tr>
<td>Lithogenics</td>
<td>7.36</td>
<td>6.36</td>
<td>10</td>
</tr>
<tr>
<td>CaCO$_3$</td>
<td>7.48</td>
<td>5.95</td>
<td>33.3</td>
</tr>
<tr>
<td>Fe(OH)$_3$</td>
<td>8.52</td>
<td>7.47</td>
<td>11.2</td>
</tr>
<tr>
<td>MnO$_2$</td>
<td>9.07</td>
<td>8.33</td>
<td>5.5</td>
</tr>
<tr>
<td><strong>EPZT Background</strong></td>
<td>7.78</td>
<td>6.62</td>
<td>14.41</td>
</tr>
<tr>
<td><strong>EPZT Plume</strong></td>
<td>8.74</td>
<td>8.01</td>
<td>5.38</td>
</tr>
<tr>
<td><strong>TAG Plume</strong></td>
<td>8.26</td>
<td>7.15</td>
<td>9.59</td>
</tr>
</tbody>
</table>

the adsorption of dissolved trace metals onto particle surfaces (Anderson et al. 1983b; Balistrieri and Murray 1986). Since then, it has been shown that despite making up a small fraction of the total suspended material throughout most of the ocean, Mn and Fe (oxyhydr-)oxide particles play an outsized role in scavenging $^{230}$Th and $^{231}$Pa. Both experimental (Geibert and Usbeck 2004) and observational (Anderson et al. 1983b; Hayes et al. 2015b; Roy-Barman et al. 2009) studies have found that the $K_d$ of MnO$_2$ is at least an order of magnitude greater than that of other constituents (e.g. CaCO$_3$ and lithogenics for both protactinium and thorium. Performing a nonlinear least squares regression to solve for endmember $K_d$ values of six particle constituents (POM, CaCO$_3$, lithogenics, opal, Fe(OH)$_3$, and MnO$_2$, Hayes et al. 2015b found that the $K_d$ of iron oxyhydroxides was an order of magnitude greater than that of POM, CaCO$_3$, and lithogenics, and that the $K_d$ of manganese oxides was an order of magnitude greater than that of iron oxyhydroxides. Hydrothermal vent fluids are highly enriched in Fe and Mn (Klinkhammer et al. 1977; Von Damm et al. 1985). When these reducing vent fluids are released into high-O$_2$ seawater, the dissolved Fe (that does not precipitate out as sulfides) and Mn oxide (Mottl and
McConachy 1990) to form particles with a high capacity for scavenging trace elements from seawater (German et al. 1990; Kadko et al. 1994). We investigate the role of iron and manganese oxides in scavenging $^{230}$Th and $^{231}$Pa using calculated distribution coefficients and fractionation factors along GP16, observed variations in particle mass, particulate iron oxyhydroxide and manganese oxide concentrations (Lam et al. 2018), together with the endmember $K_d$ values and fractionation factors for iron and manganese oxides from Hayes et al. (2015b).

Near 1500 m depth on GP16, above the plume, bulk log($K_d$) values range from 7.4-7.8 for thorium, and 6.2-6.5 for protactinium, with fractionation factors of 14-16 (Figure 1.8). Within the depth range of the plume at stations closest to the EPR ridge axis (Stations 18–21), the log ($K_d$) increases to 8.2–8.8 for thorium and 7.4–8 for protactinium, while the fractionation factor decreases to 4–5.5 (Figures 1.8 and 1.9). As the plume moves west beyond station 21, the $K_d$’s of both thorium and protactinium decrease and the fractionation factor increases towards background levels by station 36 (Figure 1.9). The maximum log($K_d$) values observed for $^{230}$Th nearly match the endmember $K_d$ value of 8.5 for iron oxyhydroxides (Table 1.1). However, the log($K_d$) values of $^{231}$Pa at stations 18–21 are regularly around 7.7, with a maximum of nearly 8.0 (Figure 1.8). Endmember log($K_d$) values for $^{231}$Pa of 7.46 for iron oxyhydroxides and 8.32 for manganese oxides imply that a much greater fraction of $^{231}$Pa is scavenged by manganese oxides compared to $^{230}$Th, which is primarily scavenged by Fe oxyhydroxides (Table 1.1). This is supported by the observed fractionation factors, which are at or just below 5, similar to the endmember fractionation factors for MnO$_2$ of 5.5 and POM of 4.9, and much lower than the Fe(OH)$_3$ endmember fractionation factor of 11.2 (Hayes et al. 2015b). We propose two hypotheses that could
Figure 1.8: Profiles, in μg/l, of Fe(OH)$_3$, MnO$_2$, and SPM in the 0.8–51 μm fraction (A–C), >51 μm size fraction (D–F), and profiles of the logarithm of distribution coefficients for $^{230}$Th (G), $^{231}$Pa (H), and fractionation factor calculated for the 0.8–51μm particle size fraction (I). Error bars indicate 1-sigma uncertainty. In A), B), D), E) and I), where error bars are not visible, uncertainties are smaller than the symbol size. In C), F), G), and H), a single error bar shows the average uncertainty for samples in the hydrothermal plume, between 2200 and 2800 m depth.
Figure 1.9: Sections of A) log $K_d$(Th), B) log $K_d$(Pa) and C) Fractionation factor.

explain the observed $K_d$, F, and particle composition and concentration data. The first is that $^{230}$Th and $^{231}$Pa are scavenged by direct adsorption onto metal oxide surfaces. The second is that ligands binding dissolved $^{230}$Th and $^{231}$Pa are co-precipitated during Fe and Mn oxide formation, along with the radionuclides they chelate. We consider the evidence for and potential implications of these two hypotheses below.

1.3.2.2 Direct Scavenging by Metal Oxide Particles

The similarity of the $K_d$ values of $^{230}$Th and $^{231}$Pa for a mixture of iron oxyhydroxide and manganese oxides, described above, supports direct adsorption to metal oxide surfaces. This hypothesis is also supported by comparison to $K_d$ values and particle composition observed at the TAG hydrothermal vent site sampled on the GEOTRACES GA03 section (Station GT11-16) in the North Atlantic. At TAG, dissolved (Hatta et al. 2015) and particulate (Lam et al. 2015) Mn/Fe ratios are both lower than at Stations 18 and 20 on GP16. There was no evidence for MnO$_2$ precipitation at TAG, but there were direct measurements of abundant iron oxyhydroxides (Lam et al. 2015). The lack of MnO$_2$ precipitation at TAG was previously observed by Trocine and Trefry (1988), and likely reflects the slow
oxidation kinetics of Mn and the young age (2 days) of the TAG plume (Kipp et al. 2018b). The log $K_d$ values for $^{230}$Th and $^{231}$Pa at TAG reach maxima of 8.26 and 7.15, respectively, while the minimum observed fractionation factor is 9.59 (Hayes et al. 2015b). The TAG $K_d$ values are lower and the fractionation factor higher than observed at Stations 18 and 20 on GP16. The fractionation factor is much closer to the Fe(OH)$_3$ endmember, indicating that iron is the primary scavenger at TAG, with manganese playing a diminished role due to the lack of Mn particles. At GP16, the higher particulate Mn/Fe ratio results in a greater relative contribution of Mn particles to scavenging of trace metals in the hydrothermal plume, and less fractionation of Th from Pa in comparison to TAG. Additionally, on GP16, Station 18 has more particulate Fe(OH)$_3$ relative to station 20, but less MnO$_2$ relative to station 20 (Figure 1.8). The particulate $^{231}$Pa/$^{230}$Th activity ratio (Figure 1.3) increases coincident with the increase in MnO$_2$ from station 18 to 20 (Figure 1.8), reflecting the greater scavenging affinity of Mn for $^{231}$Pa relative to other particulate phases. The $K_d$ values of both $^{230}$Th and $^{231}$Pa also increase from Station 18 to 20 (Figure 1.8), moving towards the higher $K_d$ endmember of MnO$_2$. Together, these findings constitute strong evidence for direct adsorption to metal oxide surfaces, though not unequivocal.

There remain features that are difficult to explain if metal oxides are directly responsible for scavenging $^{230}$Th and $^{231}$Pa. SPM, Fe(OH)$_3$, and MnO$_2$ concentrations all decrease sharply between station 20 and station 21 (Figure 1.8). Yet the $K_d$ values of $^{230}$Th and $^{231}$Pa at station 21 are greater than those of station 18, and nearly as high as at station 20 (Figure 1.8). Even at stations 25 and 26, far beyond where most of the metal oxides and SPM have been removed from the plume, $K_d$ values remain anomalously high compared to background values (Figure 1.9). At stations beyond 20, where SPM, Fe(OH)$_3$, and
MnO₂ have all precipitously declined, how can the scavenging signature of metal oxides be maintained? We propose that even after most of the particle mass has been removed, the surface area of the particles remaining in the hydrothermal plume is predominantly metal surface coatings, predominantly Mn. The high $K_d$ values at station 21, where the mass of particulate Fe(OH)_3 and Mn have sharply fallen (Figure 1.8), requires that much of the high particulate Fe(OH)_3 and Mn mass at stations 18 and 20 must be bound within the inner matrix of particles, and, with no surface functional groups exposed to seawater, cannot bind solutes like $^{230}$Th and $^{231}$Pa. This is consistent with the size fractionation of...
Mn observed by Lee et al. (2018), where 50% of the particulate Mn is predominantly in the > 51μm size fraction at stations 18 and 20, then decreases to 10–20% in the >51 μm size fraction by station 21. Preliminary synchrotron X-ray microprobe results show that pMn in hydrothermal plume particles near the vent exist as a mixture of discrete Mn(IV)-oxide particles and fine-coatings of an unidentified Mn-mineral (Lee and Lam, unpublished). We hypothesize that this latter form of nanoparticulate Mn coating could dominate the far-field particles. These combined effects would explain why there is little correlation between the mass of Fe(OH)₃ or MnO₂ with the K₅ values for ²³⁰Th and ²³¹Pa (Figure 1.10). It also might help explain the decoupling of hydrothermal plumes and benthic nepheloid layers from the inverse relationship between SPM and K₅ values for ²³⁰Th and ²³¹Pa as observed in the Atlantic Ocean (Hayes et al. 2015b). Environments with high authigenic Mn precipitation will cause particles to have anomalously high fractions of their surface areas coated by nanoparticulate Mn relative to the mass of MnO₂ and the mass of particles present, causing the K₅ values to be elevated.

Fractionation factors at 2500 m remain near 5 all the way to station 28, increasing towards background values by station 36 (Figure 1.9). Even as K₅ values have begun to fall by stations 25 and 26, low fractionation factors are maintained. The particulate MnO₂/Fe(OH)₃ ratio increases continuously from stations 25–34 (Figure 1.10), which is difficult to reconcile with the conventional understanding of oxidation kinetics, wherein the oxidation of Fe(II) (e.g. Field and Sherrell 2000) is much faster than the oxidation of Mn(II) (e.g. Cowen et al. 1990) in hydrothermal plumes. This may be related to the size partitioning and speciation of Mn and Fe in the GP16 hydrothermal plume. A significant fraction of operationally defined dissolved iron in hydrothermal plumes has been shown
to exist as large colloids, rather than in a truly soluble phase (Fitzsimmons et al. 2014). In hydrothermal plumes, the dissolved-particulate partitioning of iron may be dictated by the kinetics of colloid aggregation-disaggregation (Fitzsimmons et al. 2017), while the dissolved-particulate partitioning of manganese may be more directly a function of oxidation kinetics, perhaps hastened by microbial activity (Cowen and Bruland 1985; Cowen et al. 1986). On samples from the GP16 section, Fitzsimmons et al. (2017) found 63 ± 10% of dissolved Fe was colloidal, while only 2 ± 2% of dissolved Mn was colloidal. Colloid-bound Fe that aggregates into particles may not have the same surface area available for scavenging as nanoparticulate Mn mineral coatings on particles.

Slow, continuous precipitation of dissolved Mn controlling scavenging could cause fractionation factors close to that of MnO₂ to be maintained even in the distal plume, away from the highest pMn concentrations. This is supported by the depths of peak Fe, Mn, Th, and Pa concentrations. The depths of minimum dissolved and maximum particulate ²³⁰⁶Th and ²³¹⁶Pa change very little over the course of the hydrothermal plume. Both pFe and dFe maxima are observed to sink nearly 350 m over the 4300 km length of the plume, however dMn and pMn peaks do not (Fitzsimmons et al. 2017). This supports a decoupling of ²³⁰⁶Th and ²³¹⁶Pa scavenging from the colloidal aggregation-disaggregation kinetics governing Fe in the hydrothermal plume, and an association of ²³⁰⁶Th and ²³¹⁶Pa scavenging with the precipitation of dMn into a non-sinking particulate phase.

However, hydrothermal maxima in both dissolved and particulate ²³¹⁶Pa/²³⁰⁶Th activity ratios (Figure 1.3) require a more rapid loss of thorium relative to protactinium in the near-field hydrothermal plume. If metal oxides are directly responsible for scavenging ²³⁰⁶Th and ²³¹⁶Pa, one way this could be explained is by ²³⁰⁶Th being preferentially bound by
Fe(OH)$_3$ particles and $^{231}$Pa being preferentially scavenged by MnO$_2$ particles in the region closest to the ridge crest. Maxima in both the dissolved and particulate $^{231}$Pa/$^{230}$Th activity ratios require more rapid removal of Th-binding Fe particles relative to Pa-binding Mn particles. Iron is thought to rapidly precipitate as sulfides and oxyhydroxides in the first days after eruption of hydrothermal plumes (Mottl and McConachy 1990; Rudnicki and Elderfield 1993; Trocine and Trefry 1988), while manganese is less dynamic in this time interval (German and Seyfried 2014). Given the high dissolved and particulate $^{231}$Pa/$^{230}$Th activity ratios observed at station 18 (at the EPR), this would require preferential scavenging (adsorption and loss by sedimentation) of $^{230}$Th in the buoyant plume – as the result of rapid precipitation of iron particles. This supports modeling efforts to explain the particulate Th/Fe ratios observed in neutrally buoyant plume samples (German et al. 1991) at TAG, which required rapid scavenging rates for thorium early in the history of the hydrothermal plume (Rudnicki and Elderfield 1993).

1.3.2.3 Indirect Scavenging by Ligand Co-Precipitation

An abundance of evidence leads us to consider scavenging of $^{230}$Th and $^{231}$Pa to most likely be the result of direct adsorption to MnO$_2$ and Fe(OH)$_3$ surface functional groups for reasons described in the preceding sections. However, the results are not unequivocal, and could also be explained by the uptake and co-precipitation of ligands binding $^{230}$Th and $^{231}$Pa in solution. The low fractionation factors as far west as station 28 observed on GP16 (Figure 1.9), are similar to the endmember F values of POM (Hayes et al. 2015b), but the inferred endmember $K_d$ values for both $^{230}$Th and $^{231}$Pa are orders of magnitude lower for POM ($\log K_d = 6.5$ and 5.8, respectively) compared to Fe(OH)$_3$ and MnO$_2$ end-
members, and compared to the observed $K_d$ values in the hydro-thermal plume on GP16 (Figure 1.9). Ligands that bind thorium in solution are thought, at least to first order, to be similar to ligands which bind iron (Barbeau et al. 2001). On the GA03 section in the North Atlantic, iron-binding ligands were higher at the TAG hydrothermal vent site than in ambient deep ocean waters (Buck et al. 2015). Iron-binding ligands are often abundant in neutrally buoyant hydrothermal plumes (Bennett et al. 2008; Sander and Koschinsky 2011), occasionally in excess of the labile iron concentrations (Kleint et al. 2016) and are hypothesized to be a major factor in stabilizing dissolved Fe as plumes advect far away from vent sites (“Measuring the form of iron in hydrothermal plume particles”; Toner et al. 2009). On the GP16 section, biogeochemical ocean models were unable to reproduce the observed distribution of dissolved Fe west of the EPR without an equimolar hydrothermal input of ligands as well as iron (Resing et al. 2015).

The $K_d$ values for Th and Pa in the plume are orders of magnitude larger than for POM. For $^{230}$Th and $^{231}$Pa scavenging to be due to co-precipitation of ligands would therefore require the confluence of several factors. The observed $K_d$ values on GP16 would require that co-precipitation of ligands occurs by metal oxides stripping Th- and Pa- binding ligands out of solution with the metals still bound to them. This would have to happen while not subsequently affecting POM. The distribution coefficients of the Th- and Pa- binding ligands would have to have binding constants for Th and Pa that, when combined with the adsorption constants to metal oxides of those ligands, result in observed fractionation factors within the plume that are similar to POM. While not impossible, it would require quite a few coincidences in the values of largely unconstrained variables for the observed fractionation factors to be due to ligand scavenging.
Fitzsimmons et al. (2017) argue that iron scavenging on GP16 reflects aggregation-disaggregation of iron-binding ligands. If iron binding ligands and thorium binding ligands are roughly similar in composition (Barbeau et al. 2001), then the observed evolution of particulate \(^{230}\text{Th}\) and \(^{231}\text{Pa}\) may reflect the rate of ligand scavenging from seawater, and provide constraints on ligand removal. In global iron models with dynamic ligands, the loss fluxes of ligands due to aggregation and/or scavenging are either completely unconstrained by data (Völker and Tagliabue 2015) or not included (Misumi et al. 2013). While we prefer the interpretation that adsorption of \(^{230}\text{Th}\) and \(^{231}\text{Pa}\) occurs as a result of direct scavenging to metal oxides, we hesitate to rule out the role of ligands completely, and believe that the distribution of thorium isotopes might be used to understand some of the dynamic processes involved in hydrothermal iron-binding ligand production, aggregation, and destruction. One way this might be achieved is by analyzing hydrothermal particles for the concentrations and structures (e.g. Boiteau et al. 2013) of ligands present to determine if co-precipitation of metal oxide particles scavenges dissolved metal-binding ligands from solution. Another might be to apply the method used by Kipp et al. (2018b) to evaluate the loss rate of dissolved Fe to calculate the loss rate of dissolved L1 ligands across the GP16 section to determine the linkage between iron loss to particles with L1 ligand loss. Given their potential influence on trace metal scavenging and the stabilization of dissolved forms of iron, testing the destruction mechanisms of ligands in hydrothermal plumes would be a valuable topic for future work.
1.3.3 Where and when does Scavenging Occur?

Where scavenging occurs relative to the input of hydrothermal material is critical for understanding the local mass balance and sedimentary input of trace metals. Several studies have attempted to connect the concentrations of $^{230}$Th and $^{231}$Pa in ridge flank sediments to variations in hydrothermal activity through time (Frank et al. 1994; German et al. 1993, 1997; Lund and Asimow 2011; Shimmield and Price 1988). To better understand the effects of hydrothermal activity on the location of $^{230}$Th and $^{231}$Pa removal from the water column, we construct tracer-tracer plots of dissolved $^{3}$He$_{xs}$ (Jenkins et al. 2018) with dissolved, particulate, and total $^{230}$Th and $^{231}$Pa (Figure 1.11). Both tracers are shown in terms of inventories, integrated from 2200 to 2800 m. Similarly to Resing et al. (2015), our integrations at station 18 only go to 2640 m for $^{3}$He$_{xs}$ and dissolved $^{230}$Th and $^{231}$Pa, and to 2610 m for particulate and total activities of $^{230}$Th and $^{231}$Pa. Since we lack particulate samples between 300 m and 2400 m depth at station 34, we do not calculate inventories of particulate or total $^{230}$Th and $^{231}$Pa there. With the exception of stations 18 and 23, the dissolved and total inventories of $^{230}$Th and $^{231}$Pa tend to increase (Figure 1.11), while the particulate inventories of $^{230}$Th and $^{231}$Pa decrease at stations progressively further west of the EPR.

Tracer-tracer plots utilize curvature as a signal for scavenging and removal (German et al. 1990, 1991; Rudnicki and Elderfield 1993). If an element or isotope forms a straight line with regard to a conservative tracer, then, disregarding potential changes in endmember tracer concentrations, mixing and dilution away from a hydrothermal source would be the only process accounting for the co-variation of the two elements. These relationships
Figure 1.11: Cross plots of radionuclide inventories (2200–2800 m depth interval) with hydrothermal $^{3}$He (Jenkins et al., 2017). From left to right: $^{230}$Th, $^{231}$Pa $^{x}$s, and $^{x}$s $^{231}$Pa/$^{230}$Th activity ratio. Top row: dissolved inventories. Middle row: Particulate inventories. Bottom row: total inventories.

become more difficult for $^{230}$Th and $^{231}$Pa, which have multiple in-situ sources.

Ingrowth from uranium decay causes dissolved inventories of $^{230}$Th and $^{231}$Pa to increase away from the ridge axis as a function of plume age. Scavenging would act to lower the slope of that increase with time, and also add a significant source for the mass
budget of particulate plume inventories of $^{230}$Th and $^{231}$Pa. In addition, there is a net source of $^{230}$Th and $^{231}$Pa to the hydrothermal plume as it moves west via desorption from particles settling from the sea surface, which carry higher $^{230}$Th and $^{231}$Pa activities than the waters within the plume.

Particulate $^{230}$Th and $^{231}$Pa inventories are positively correlated with $^3$He$_{xs}$, with the exception of station 18 (Figure 1.11d-e). After station 20, the particulate radionuclide inventories decline rapidly towards station 21, then, with the exception of station 23 which is thought to be a recirculation feature that disrupts the continuous westward aging of the plume (Jenkins et al. 2018), decline towards station 36 with concave upward shape relative to $^3$He$_{xs}$. If the particulate inventories were governed solely by adsorption of $^{230}$Th and $^{231}$Pa either ingrown from uranium decay or desorbed from surface particles, we would expect their inventories to be convex upward with respect to $^3$He$_{xs}$. Qualitatively, the concave upward relationships between $^{230}$Th and $^{231}$Pa inventories with $^3$He$_{xs}$ (Figure 1.11d-e) support continuous net removal of particulate $^{230}$Th and $^{231}$Pa throughout the plume.

We construct a simple mass balance to test whether dissolved $^{230}$Th and $^{231}$Pa are continuously scavenged over the entire area of the hydrothermal plume observed on GP16. To show net removal from the plume, we only need to prescribe two sources as the plume moves west: ingrowth by uranium decay and desorption from surface-derived particles falling into the hydrothermal plume. Not included is dilution of plume waters by mixing, an issue we will return to later.

While the production rate of $^{230}$Th and $^{231}$Pa by uranium decay is well-known, it is not straightforward to calculate the desorption flux of $^{230}$Th and $^{231}$Pa from sinking surface-derived particles. These particles are in equilibrium with respect to adsorption and des-
ortion with waters directly above the plume, which have higher dissolved $^{230}\text{Th}$ and $^{231}\text{Pa}$ concentrations than in the plume. Thus, to come into equilibrium within the plume, the surface-derived particles will lose Th and Pa to the dissolved phase via desorption. We estimate the net supply of dissolved $^{230}\text{Th}$ and $^{231}\text{Pa}$ by desorption as the difference between the flux of particulate $^{230}\text{Th}$ and $^{231}\text{Pa}$ falling into the plume on surface-derived particles and the flux of particulate $^{230}\text{Th}$ and $^{231}\text{Pa}$ leaving the plume on surface-derived particles.

Given previous estimates of desorption rate constants for thorium of $0.1–10\text{ yr}^{-1}$ (Bacon and Anderson 1982; Lerner et al. 2016; Murnane et al. 1994) and bulk particle sinking rates of 300–900 m/yr (Lerner et al. 2016), we infer that the entire flux of particulate $^{230}\text{Th}$ and $^{231}\text{Pa}$ is desorbed at least once during the lifetime of surface-derived particles within the hydrothermal plume. Away from features that lead to convergence or divergence of the lateral flux of $^{230}\text{Th}$ and $^{231}\text{Pa}$ by mixing, such as boundary scavenging, and given a uniform particle field, the downward flux ($F$) of particulate $^{230}\text{Th}$ and $^{231}\text{Pa}$ through any depth horizon ($z$) is equal to the integrated production by uranium decay in the overlying water column:

$$F_z = \beta \ast z$$

(1.5)

Here, $\beta$ is the known production rate of $^{230}\text{Th}$ or $^{231}\text{Pa}$, in units of activity/m$^2$/yr. We can treat the integrated production in the overlying water column as the source term for gross desorption of particulate $^{230}\text{Th}$ and $^{231}\text{Pa}$ from surface-derived particles.

Adsorption of dissolved $^{230}\text{Th}$ and $^{231}\text{Pa}$ onto surface-derived particles will also occur within the hydrothermal plume. Net desorption must be estimated as the difference between supply of dissolved $^{230}\text{Th}$ by desorption from surface-derived particles and loss by
adsorption onto them and subsequent sedimentation. Equation (1.5) provides a way to calculate the sinking flux of particulate $^{230}$Th and $^{231}$Pa into the plume. With reversible scavenging, $F_z$ is also directly proportional to the activity of dissolved $^{230}$Th or $^{231}$Pa at the depth $z$, $A_z$:

$$ F_z = A_z \times U $$  \hspace{1cm} (1.6)

$U$ is a constant proportional to particle flux, in units m/yr. Assuming for now that there is no change in the properties of surface-derived particles as they fall through the hydrothermal plume, we can evaluate the adsorption of dissolved $^{230}$Th and $^{231}$Pa at the depth of their minimum dissolved activities as:

$$ F_{\text{min}} = A_{\text{min}} \times U $$  \hspace{1cm} (1.7)

To calculate $F_{\text{min}}$, we first determine the value of $U$ above the plume by combining Equations 1.5 and 1.6 at the depth of 2200 m:

$$ F_{2200} = A_{2200} \times U $$  \hspace{1cm} (1.8)

Rearranging, we solve for $U$ as:

$$ U = \frac{\beta \times 2200}{A_{2200}} $$  \hspace{1cm} (1.9)

After having solved for $U$, we can solve for the loss of dissolved $^{230}$Th and $^{231}$Pa from the plume by adsorption onto surface-derived particles using Equation (1.7). The net supply of $^{230}$Th and $^{231}$Pa ($F_{\text{des}}$, units activity/m$^2$/yr) within the plume by desorption from surface-
derived particles, at each station, is then:

\[ F_{\text{des}} = F_{2200} - F_{\text{min}} \]  

Before continuing to the mass balance, we return to our assumption that the adsorptive capabilities of surface-derived particles do not change within the depth range of the plume. In fact, surface particles are likely to be coated by precipitating Fe(OH)$_3$ and/or MnO$_2$ during their transit, as described in Section 1.3.2.2, which would alter the sorptive properties of surface functional groups on the particles. However, we can conceptually treat Fe(OH)$_3$ and MnO$_2$ coatings on surface-derived particles as plume particles. As a result, our assumption of no change in the adsorptive properties of surface-derived particles represents an upper limit to their contribution to scavenging loss of $^{230}$Th and $^{231}$Pa from the hydrothermal plume. In our overall mass balance within the plume, removal of $^{230}$Th and $^{231}$Pa would therefore be a minimum estimate.

We can write a mass balance for the inventories (I, units Bq/m$^2$) of $^{230}$Th and $^{231}$Pa within the hydrothermal plume as follows:

\[ \frac{dI}{dt} = \beta + F_{\text{des}} - F_{\text{scav}} \]  

$\beta$ is the production rate from uranium decay integrated across 600 m and $F_{\text{des}}$ is the net desorption from surface-derived particles into the hydrothermal plume. Both of these components have units of Bq/m$^2$/yr. We can calculate the change in time (dt) between stations by dividing the westward distance component ($\Delta x$) between each station by a
water mass velocity (v) of 0.4 cm/s (Hautala and Riser 1993). After discretizing and re-arranging, our final mass balance model for the westward evolution of \(^{230}\text{Th}\) and \(^{231}\text{Pa}\) in the hydrothermal plume can be written:

\[
I_{\text{stn}} = I_{\text{prev}} + (\beta + F_{\text{des}}) \frac{\Delta x}{v}
\]  

(1.12)

\(I_{\text{stn}}\) is the modeled inventory of \(^{230}\text{Th}\) or \(^{231}\text{Pa}\) being solved for at a given station, and \(I_{\text{prev}}\) is the modeled inventory at the closest station to the east. Before discussing the results of the model, it is critical to acknowledge that we purposefully neglect mixing as a source of \(^{230}\text{Th}\) and \(^{231}\text{Pa}\) to the hydrothermal plume. Mixing of depleted plume waters with ambient, non-plume deep water would serve as a third source of \(^{230}\text{Th}\) and \(^{231}\text{Pa}\). However, we cannot adequately constrain the rates of mixing. Therefore, for our preliminary mass balance, we leave out the effects of mixing.

We find that, for \(^{230}\text{Th}\), production alone slightly over predicts the observed inventories of \(^{230}\text{Th}\) west of the EPR (Figure 1.12). With desorption added in, the modeled \(^{230}\text{Th}\) inventories are much greater than the observed inventories. This means that continuous scavenging onto plume-derived particles must be happening within the hydrothermal plume, sufficient to balance desorption of \(^{230}\text{Th}\) from particles falling in from above and any other sources of Th to the hydrothermal plume, such as mixing with non-plume waters, which would serve as a net source. As a result, the amount of \(^{230}\text{Th}\) falling to the sediments beneath stations west of the EPR would roughly balance production in the entire overlying water column. Our model therefore indicates that in sediments hundreds to thousands of kilometers downstream of hydrothermal venting, the use of \(^{230}\text{Th}\) as a
Figure 1.12: Mass Balance Modeled and Observed Inventories of $^{230}$Th or $^{231}$Pa at stations west of the EPR. Red dashed lines show models with ingrowth from uranium decay as the only source, and solid blue lines show models with additional desorption flux.
constant flux proxy for deriving sediment mass accumulation rates (e.g. Francois et al. 2004) is valid. For \(^{231}\)Pa, production alone cannot account for the increase moving west of the EPR. Only after the desorption flux is added does the modeled \(^{231}\)Pa become greater than the observed inventories. The hydrothermal scavenging removal of \(^{231}\)Pa is thus less than the desorption flux, and the amount of \(^{231}\)Pa reaching the sediments would be less than production in the entire overlying water column.

1.4 Differential Scavenging Behavior of \(^{232}\)Th

Until now, our discussion of the behavior in thorium in the hydrothermal plume observed on GP16 has focused on radiogenic \(^{230}\)Th. It is generally assumed that, since they have the same valence shell, neither has a known biological use, and thorium does not participate in redox reactions, the scavenging dynamics of \(^{232}\)Th and \(^{230}\)Th should be identical. This assumption is critical in applying the removal residence time derived from measuring \(^{230}\)Th to \(^{232}\)Th for calculating dust fluxes (Deng et al. 2014; Hayes et al. 2013b, 2015c; Lopez et al. 2015), boundary exchange fluxes (Hayes et al. 2013b), and potentially to benthic nepheloid layers (Bacon and Loeff 1989; Rutgers van der Loeff et al. 2002). Differential incorporation into colloids has been proposed as a potential mechanism by which to fractionate \(^{232}\)Th from \(^{230}\)Th; however, the only studies with measurements of colloidal \(^{232}\)Th and \(^{230}\)Th have found that both isotopes have a similar fraction of their dissolved concentration as colloids (Hayes et al. 2015c, 2017; Roy-Barman et al. 2002). For particle-reactive nuclides like \(^{232}\)Th with surface and ocean bottom sources, rather than an in-situ source from radioactive decay, the 1-d profile expected from reversible scavenging would be a constant value
throughout the water column (Bacon and Anderson 1982). Reversibly scavenged nuclides with in-situ sources from uranium decay ($^{230}$Th, $^{231}$Pa) would be expected to increase linearly with depth (Bacon and Anderson 1982). Therefore, under reversible scavenging conditions, the $^{232}$Th/$^{230}$Th ratio would decrease with depth. Typically, $^{232}$Th concentrations are constant below 1000 m (Hayes et al. 2013b), meaning that decreases in the $^{232}$Th/$^{230}$Th ratio due to reversible scavenging are observed below that depth. If $^{232}$Th and $^{230}$Th were scavenged identically in the GP16 hydrothermal plume, then we would expect that the observed trend of decreasing $^{232}$Th/$^{230}$Th with depth in the overlying water column would continue through the plume.
On GP16, the dissolved $^{232}\text{Th}/^{230}\text{Th}$ ratio decreases slightly throughout the water column from 1000 to 2000 m depth, as expected from reversible scavenging, before rapidly increasing to a maximum within the hydrothermal plume (Figure 1.13). The highest plume $^{232}\text{Th}/^{230}\text{Th}$ ratios are observed at stations closest to the ridge axis, with $^{232}\text{Th}/^{230}\text{Th}$ ratios decreasing westward, with the exception of a high $^{232}\text{Th}/^{230}\text{Th}$ ratio observed at station 26 (Figure 1.13). The maximum in $^{232}\text{Th}/^{230}\text{Th}$ ratio likely reflects a plume source of dissolved $^{232}\text{Th}$ that reacts differently with particles compared to $^{230}\text{Th}$. We can test this hypothesis by calculating the amount of additional $^{232}\text{Th}$ in the plume compared to what is expected from reversible scavenging (Figure 1.4b). In the presence of intense scavenging in the hydrothermal plume, we would expect $^{232}\text{Th}$ to experience the same degree of depletion, relative to reversible scavenging, as $^{230}\text{Th}$ does. To calculate the amount of additional unreactive $^{232}\text{Th}$ added in the hydrothermal plume, we first determine the expected concentration of $^{232}\text{Th}$ if it experienced the same degree of scavenging as $^{230}\text{Th}$:

$$^{232}\text{Th}_{\text{exp}} = ^{232}\text{Th}_{\text{rev}} \times (1 - \% \text{depletion})$$  \hspace{1cm} (1.13)

$^{232}\text{Th}_{\text{rev}}$ is defined as the concentration of dissolved $^{232}\text{Th}$ expected from reversible scavenging. We use the concentration of $^{232}\text{Th}$ at 2200 m depth at each station, just above the hydrothermal plume, as the value for $^{232}\text{Th}_{\text{rev}}$. The % depletion term is derived from the % depletion calculated using Equation 1.1, but with dissolved instead of total ($^{230}\text{Th}_{\text{xs}}$). We then integrate the measurements of dissolved $^{232}\text{Th} (^{232}\text{Th}_{\text{meas}})$ within the hydrothermal plume at each station to calculate the observed inventory of $^{232}\text{Th} (^{232}\text{Th}_{\text{obs}})$ present within
Figure 1.14: Hydrothermal-sourced \(^{232}\text{Th}_{\text{add}}\) inventories plotted against hydrothermal \(^3\text{He}\) \(^3\text{He}_{\text{xs}}\) inventory within the plume (2200–2800 m depth interval). Each point corresponds to a full-depth station (Figure 1.1). B) \(^{232}\text{Th}_{\text{add}}/^{3}\text{He}_{\text{xs}}\) inventory ratios plotted against longitude, showing a nearly constant ratio between stations 18–32 (except 26), before decreasing at stations 34 and 36.

\[
^{232}\text{Th}_{\text{obs}} = \int_{2200}^{2800} \frac{^{232}\text{Th}_{\text{meas}}}{\text{mol/m}^2} dz \tag{1.14}
\]

The extra \(^{232}\text{Th}\) \(^{232}\text{Th}_{\text{add}}\) is simply the difference between the observed inventory of \(^{232}\text{Th}\) and the amount expected from reversible scavenging:

\[
^{232}\text{Th}_{\text{add}} = ^{232}\text{Th}_{\text{obs}} - ^{232}\text{Th}_{\text{exp}} \tag{1.15}
\]

Stations with low (high) \(^{232}\text{Th}_{\text{add}}\) would have high (low) observed \(^{232}\text{Th}\), low (high) \(^{232}\text{Th}\) at 2200 m, or high (low) percent depletion of \(^{230}\text{Th}\).

If our hypothesis that \(^{232}\text{Th}_{\text{add}}\) reflects an unreactive hydrothermal \(^{232}\text{Th}\) source is correct, then we would expect to see that it has a constant, positively correlated slope with
$^{3}$He$_{xs}$, with decreasing concentrations of both moving away from the ridge axis. An unreactive pool of dissolved $^{232}$Th would have to be stabilized in the colloidal phase. Colloids are still removed by aggregation and sinking, so if the $^{232}$Th$_{add}/^{3}$He$_{xs}$ ratio decreased across the transect, with a maximum near the ridge axis, then this might indicate $^{232}$Th in a colloidal phase undergoing aggregation and removal from the dissolved phase. With the exception of station 26, which had unexpectedly high $^{232}$Th/$^{230}$Th ratios within the plume, $^{232}$Th$_{add}$ decreases linearly away from the ridge from stations 18-32 (Figure 1.14a), with a constant ratio to $^{3}$He$_{xs}$ (Figure 1.14b). We believe this is strong evidence for a ridge crest source of unreactive, colloidal $^{232}$Th. Interestingly, there is a decrease in the $^{232}$Th$_{add}/^{3}$He$_{xs}$ ratio at stations 34 and 36 (Figure 1.14b). This may reflect an increase in the aggregation and removal rate of the $^{232}$Th-binding colloids, more efficient scavenging of colloids by greater biogenic particle flux raining into the plume from the overlying water column (Black et al. 2018), or second-order reaction kinetics of colloid aggregation.

Assuming that the constant $^{232}$Th$_{add}/^{3}$He$_{xs}$ ratio reflects the ratio being erupted at the ridge axis, we can determine the flux of hydrothermal $^{232}$Th to the oceans. We regress $^{232}$Th$_{add}$ against $^{3}$He$_{xs}$, for stations 20–32, not including station 26 (n=7), to find a $^{232}$Th$_{add}/^{3}$He$_{xs}$ ratio of 7.14 ± 1.17 (1σ standard deviation) mol/mol. There are many estimates of the global $^{3}$He flux (Bianchi et al. 2010; Craig et al. 1975; Dutay et al. 2004; Schlitzer 2016), but for ease of comparison to other data (Resing et al. 2015; Roshan et al. 2016) from GP16, we use the 527 ± 102 mol yr$^{-1}$ estimate of Bianchi et al. (2010). Multiplying the $^{232}$Th$_{add}/^{3}$He$_{xs}$ ratio found on GP16 by the global $^{3}$He flux allows us to calculate the global $^{232}$Th flux from hydrothermal vents, which we find to be 3760 ± 950 mol yr$^{-1}$. Using a global dust deposition to the oceans of 450 Tg yr$^{-1}$ (Jickells et al. 2005), 14
Figure 1.15: Cartoon illustrating the movement of trace metals through different reservoirs (MORB, vent fluids, deep ocean hydrothermal plume) during hydrothermal circulation. Me/Th values (mol/mol) are shown for n-MORB (Gale et al. 2013), vent fluids (Chen 1987; Chen et al. 1986b), and flux ratios from the hydrothermal plume observed on GP16 (Equation 1.16).

ppm $^{232}$Th in the <5 μm fraction of dust source sediments (Kienast et al. 2016; McGee et al. 2016), and an estimate of the solubility of $^{232}$Th as 15% (Deng et al. 2014; Hayes et al. 2013b), we calculate a global input rate of dissolved $^{232}$Th from dust of $4.07 \times 10^6$ moles yr$^{-1}$. The hydrothermal flux of operationally defined dissolved, but actually unreactive colloidal $^{232}$Th is <1% of the dissolved $^{232}$Th input from dust, meaning that hydrothermal inputs constitute a negligible portion of the oceanic thorium budget.

The inferred flux of hydrothermal $^{232}$Th can be compared to those calculated for Fe, Mn (Resing et al., 2015) and Zn (Roshan et al., 2016) from GP16 data. For each metal (Me), the flux is computed by multiplying the water column Me/$^{3}$He$_{xs}$ ratio by the global $^{3}$He$_{xs}$
flux (as done for $^{232}\text{Th}_{\text{add}}$ in the previous paragraph). By taking the ratio of these fluxes to the flux of $^{232}\text{Th}_{\text{add}}$, the $^3\text{He}_{\text{xs}}$ terms cancel and we are left with the flux ratio of Fe, Mn, or Zn to $^{232}\text{Th}_{\text{add}}$ (Me/Th):

$$\frac{\text{Me/Th flux ratio}}{^{232}\text{Th}_{\text{add}}^{\text{flux}}/^{3}\text{He}_{\text{xs}}^{\text{flux}}} = \frac{\text{Me}^{\text{flux}}/^{232}\text{Th}_{\text{add}}}{^{3}\text{He}_{\text{xs}}/^{3}\text{He}_{\text{xs}}}$$  \quad (1.16)

If the colloids maintaining $^{232}\text{Th}_{\text{add}}$ in the dissolved phase are basaltic in origin, we might expect that the Fe/$^{232}\text{Th}_{\text{add}}$, Mn/$^{232}\text{Th}_{\text{add}}$, and Zn/$^{232}\text{Th}_{\text{add}}$ (together denoted Me/Th, with units mol/mol) flux ratios on GP16 are similar to the ratios found in average n-MORB (Gale et al. 2013), or to the ratios found in endmember hydrothermal vent fluids, though there are few (n=7) measurements of $^{232}\text{Th}$ concentration in vent fluids (Chen 1987; Chen et al. 1986b). To determine the mobility of these three metals relative to thorium in different stages of hydrothermal circulation, we compare the Me/Th ratios from n-MORB to hydrothermal fluids, and the Me/Th ratios of hydrothermal fluids to the dissolved Me/Th flux ratios from water column measurements in the hydrothermal plume sampled on GP16 (Figure 1.15). As hydrothermal circulation begins, seawater is heated and passes through the ocean crust (part 1 in Figure 1.15). This hot, acidic, reducing water leaches metals from the ocean crust, and becomes buoyant enough to rise towards the surface as the fluid in hydrothermal vents (part 2 in Figure 1.15). By comparing the Me/Th ratios in vent fluids with Me/Th in the ocean crust, we test the relative mobility of trace metals to thorium under the conditions of hydrothermal circulation. In hydrothermal fluids, Fe/Th is 1.5 times higher than in n-MORB, Mn/Th is 50 times higher than in n-MORB, and Zn/Th is 20,000 times higher than in n-MORB. Zn is known to be strongly enriched in hydrothermal
fluids over MORB (Von Damm et al. 1985), which drives the much greater Zn/Th ratio in fluids compared to n-MORB. The similar Fe/Th values in both fluids and n-MORB indicate that Fe and Th have similar mobility under the hot, reducing, acidic conditions under which metals are leached from ocean crust.

Vent fluids then erupt and vigorously mix with ambient seawater, resulting in the precipitation of metals as sulfides and/or oxyhydroxides (part 3 in Figure 1.15). By comparing water column Me/Th flux ratios from GP16 with those in vent fluids, we can evaluate the relative reactivity of Fe, Mn, and Zn compared to $^{232}$Th between the time of eruption and subsequent rising, mixing, and westward transit as a neutrally buoyant plume (part 4 in Figure 1.15). The dissolved Zn/Th flux ratio in the hydrothermal plume is 50 times lower than the Zn/Th ratio in hydrothermal fluids; the Fe/Th plume flux ratio is 250 times lower than in the Fe/Th of vent fluids; and the Mn/Th flux ratio is 370 times lower than the Mn/Th of vent fluids. Given that Fe and Zn are thought to rapidly precipitate out of solution as sulfides upon being erupted and reacting with seawater, it is surprising that the dissolved Zn/Th flux ratio in seawater is most enriched compared to vent fluids, and the Mn/Th ratio is the most depleted compared to vent fluids. This could reflect spatio-temporal variations in vent fluid chemistry (e.g. Yücel and Luther 2013), for example, if the endmember vent fluids from the Juan de Fuca Ridge and the EPR at 21ºN used to represent vent fluid chemistry have different Fe, Mn, and Zn concentrations than those being erupted at 15–17ºS on the EPR, which feed the hydrothermal plume sampled on GP16. Regardless of the pattern, Fe, Mn, and Zn are removed from solution much faster than $^{232}$Th$_{add}$ upon reacting with seawater.

Since $^{232}$Th$_{add}$ is in excess of what is expected from $^{230}$Th scavenging, it is unlikely that
the formation of $^{232}$Th-binding colloids happens within the water column, since those processes would likely bind $^{230}$Th as well and link the scavenging behavior of the two isotopes. Given the high affinity of dissolved Th for adsorption to MnO$_2$ and Fe(OH)$_3$, if $^{232}$Th were erupted in dissolved form, then it should have been scavenged immediately after eruption by the rapidly forming Mn and Fe oxides. If we assume that all of the $^{232}$Th$_{add}$ is released in the form of unreactive basaltic colloids, then the low Me/Th flux ratios compared to the Me/Th ratios of vent fluids would indicate that only a small fraction of dissolved Fe, Mn, and Zn are released into the water column in the same unreactive phase as Th, since if they were, the water column Me/Th ratios would be expected to stay similar to the vent fluid Me/Th ratios. Though circumstantial, we take this to be evidence that the high percentage of colloidal Fe found in hydrothermal plumes (Fitzsimmons et al. 2014) is likely bound into colloids well after being erupted into oxidizing seawater.

1.5 Summary and Conclusions

The isotopes of thorium and protactinium offer unique insights into trace metal scavenging by hydrothermal plumes particles. Deficits in the dissolved and total activities of $^{230}$Th and $^{231}$Pa within the plume were observed 4000 km away from the EPR ridge crest, indicating basin-scale signatures of hydrothermal scavenging. The timescales over which these signatures will be preserved after waters pass beyond locations of hydrothermal activity are 64 years for $^{230}$Th and 140 years for $^{231}$Pa. While we cannot rule out the potential co-precipitation of Th- and Pa- binding ligands as the driver of scavenging, the tight co-variation of Mn and Fe(OH)$_3$ particles and the distribution coefficients and fractionation
factors of $^{230}$Th and $^{231}$Pa lead us to conclude that direct adsorption to nanoparticulate metal surface sites is the mechanism for $^{230}$Th and $^{231}$Pa scavenging in the hydrothermal plume. A mass balance model for the westward evolution of the hydrothermal plume requires continuous removal of $^{230}$Th and $^{231}$Pa. For $^{230}$Th, removal balances sources other than production, such as desorption from surface-derived particles, and the amount of $^{230}$Th reaching the seafloor below the plume should be equal to production in the overlying water column. Unlike $^{230}$Th, hydrothermally-derived $^{232}$Th is not as efficiently scavenged within the dissolved phase, indicating a hydrothermal source of $^{232}$Th that is likely bound in an unreactive colloidal phase. In all of these cases, we raised several questions about the details of the scavenging, speciation, and particle dynamics that could potentially be answered by improved analytical techniques for measuring colloidal Th and Pa, future GEOTRACES sections, and future process studies.

**Acknowledgements**

This work was supported by the National Science Foundation (OCE-1233688 to LDEO, OCE-1233903 to UMN, and OCE-518110 to UCSC), as well as an NSF Graduate Research Fellowship to F.J.P (DGE-16-44869). Thanks go to the captain, crew, and scientists aboard the R/V Thomas G. Thompson, in particular the bottle and pump teams. We thank Bill Jenkins for making $^3$He data available prior to its publication. We also thank Gisela Winckler, Kassandra Costa, and Terry Plank for insightful discussions. Comments by Walter Geibert and an anonymous reviewer greatly improved the manuscript.
Chapter 2

Timescales of hydrothermal scavenging in the South Pacific

Ocean from $^{234}$Th, $^{230}$Th, and $^{228}$Th

Note: This chapter was published in the journal *Earth and Planetary Science Letters* in 2019.

Abstract

Hydrothermal activity in the deep ocean generates plumes of metal-rich particles capable of removing certain trace elements from seawater by adsorption and sedimentation. This removal process, known as scavenging, can be probed using the insoluble radiogenic isotopes of thorium (Th), which are produced at a known rate in the water column via the decay of soluble uranium ($^{234}$Th, $^{230}$Th) and radium ($^{228}$Th) isotopes. We present dissolved and particulate measurements of these three thorium isotopes in a hydrothermal plume observed in the southeast Pacific Ocean on the GEOTRACES GP16 section. Since their half-lives vary from days ($^{234}$Th) to years ($^{228}$Th) to tens of thousands of years ($^{230}$Th), the combination of their signals can be used to understand scavenging processes occurring on

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a wide range of timescales. Scavenging is a multi-step process involving adsorption and desorption onto particles, followed by particle aggregation, sinking, and eventual sedimentation. We use thorium isotopes to study how hydrothermal activity affects these steps. The rate constants for net adsorption of $^{234}$Th determined here are comparable to previous estimates from hydrothermal plumes in the Atlantic and North Pacific Oceans. The partitioning of $^{234}$Th and $^{230}$Th between large and small particles is more similar in the hydrothermal plume than above it, indicating faster aggregation of particles within the hydrothermal plume at stations nearby the East Pacific Rise than in waters outside the plume. In addition to rapid scavenging and aggregation near the ridge axis, we also infer continuous off-axis scavenging from observations and modeling of $^{228}$Th/$^{228}$Ra activity ratios. The degree of depletion of the three thorium isotopes increases in order of half-life, with total $^{234}$Th activity close to that of its parent $^{238}$U, but $^{230}$Th showing nearly 70% depletion compared to expected values from reversible scavenging. By modeling the variations in depletion for the different isotopes, we show that much of the $^{230}$Th removal is inherited from scavenging events happening long before the most recent hydrothermal inputs.

### 2.1 Introduction

Submarine hydrothermal vents emit hot, reducing fluids that are highly enriched in trace metals such as iron (Fe) and manganese (Mn) relative to the deep ocean (German and Seyfried 2014). Upon reacting with seawater, dissolved Fe and Mn precipitate to form particles, with Fe initially forming sulfides closest to the ridge axis (Feely et al. 1987),
and both Fe and Mn forming oxides over longer distances (Feely et al. 1996). These metal- 
alliferous particles have highly reactive surfaces that can readily remove trace metals, 
phosphorus, and carbon from solution (Feely et al. 1990; German et al. 2015; Kadko et al. 
1994), making hydrothermal systems important sinks for a wide range of elements in the 
ocean.

The south Pacific was identified as a major locality of hydrothermal activity by the 
discovery of volcanic $^3$He emanating from the East Pacific Rise (EPR) at 2500 m between 
15°-20°S (Lupton and Craig 1981). In 2013, the GEOTRACES GP16 cruise followed this 
south Pacific helium plume west of the EPR. In addition to $^3$He, the plume was found to 
be highly enriched in dissolved metals like Fe (dFe) and Mn (dMn) over 4000 km west of 
the EPR (Resing et al. 2015). Enrichments in particulate Fe (pFe) and Mn (pMn) were also 
found in the GP16 hydrothermal plume (Fitzsimmons et al. 2017). While pMn and dMn 
were both found to have peaks along the same isopycnal as $^3$He, the pFe and dFe peaks 
descended below the $^3$He isopycnal, indicating removal by sinking particles, despite the 
apparent conservative behavior of dFe previously inferred by Resing et al. (2015). Model-
ing studies have shown that hydrothermal Fe, stabilized in solution and carried by abyssal 
ocean circulation, could upwell and support new primary production, particularly in the 
Southern Ocean (Resing et al. 2015; Tagliabue et al. 2010). A better understanding of re-
moval processes and their associated timescales in hydrothermal plumes could potentially 
improve models of Fe stabilization and removal.

Chemical scavenging encapsulates the sum of processes responsible for the removal 
of ions from the ocean by oceanic particles. These individual processes include adsorp-
tion and desorption reactions, aggregation and disaggregation of particles, and eventually
particle settling and sedimentation at the seafloor (Bacon and Anderson 1982). Net scavenging rates responsible for the removal of elements from the ocean integrate across the rates of these individual processes.

The radiogenic isotopes of thorium ($^{234}$Th, $^{230}$Th, $^{228}$Th) are powerful tools for understanding the kinetics of oceanic scavenging processes. These thorium isotopes are produced at well-known rates in seawater by the decay of soluble uranium ($^{238}$U $\rightarrow^{234}$Th, $^{234}$U $\rightarrow^{230}$Th) and radium ($^{228}$Ra $\rightarrow^{228}$Th). Thorium is highly insoluble in seawater, with a scavenging residence time on the order of 10–40 yr in the deep ocean (Henderson and Anderson, 2003). Thorium adsorbs onto particles that subsequently settle through the water column, generating radioactive disequilibrium with respect to their more soluble parents. The rapid removal of Th is apparent from the open ocean activity ratio of $^{230}$Th to its parent $^{234}$U of ~0.00002 (Moore and Sackett 1964). With respective half-lives for $^{234}$Th, $^{230}$Th, and $^{228}$Th of 24.1 days (Knight and Macklin 1948), 75,587 yr (Cheng et al. 2013), and 1.91 yr (Kirby et al. 1956), thorium isotopes can constrain scavenging behavior in the ocean on a range of timescales spanning months to millennia. Pavia et al. (2018) studied hydrothermal scavenging of $^{230}$Th and $^{231}$Pa in the GP16 hydrothermal plume, finding large depletions in total and dissolved $^{230}$Th and $^{231}$Pa coincident with enrichments in the particulate phase. The authors determined that this intense scavenging was largely the result of iron and manganese coatings on particles, and that scavenging was continuous over the 4000 km extent of the plume. In this study, we use combined measurements of dissolved and particulate $^{234}$Th, $^{230}$Th, and $^{228}$Th and their parent activities to study the kinetics of the individual processes involved in scavenging, including adsorption and desorption, particle aggregation, and the net scavenging removal of thorium from the water column. We
use these observations to assess the importance of local and distal hydrothermal activity on $^{230}$Th scavenging previously observed in the GP16 hydrothermal plume, and to study the timescales over which different scavenging processes act in hydrothermal settings.

2.2 Materials and Methods

2.2.1 Cruise Setting

Samples were taken on board the R.V. Thomas G. Thompson during the GEOTRACES GP16 cruise (TGT303) between Ecuador and Tahiti from 25 October to 20 December, 2013. We focus on the three sampling locations at or nearest downstream of the EPR: station 18 at
the EPR and stations 20 and 21, less than 250 km to the west along 15ºS latitude (Figure 2.1). Since the hydrothermal plume was interrupted by a discontinuity due to mixing of non-plume waters at the next station to the west (Jenkins et al. 2018; Lupton and Jenkins 2017), we restrict our analysis to the three stations nearest to the EPR.

2.2.2 Sample Collection and Analysis

Dissolved $^{230}$Th and total $^{234}$Th samples were taken from Niskin bottles, with $^{230}$Th collected from bottles on a conventional steel rosette and deep $^{234}$Th samples taken from bottles hung above in-situ pumps. Dissolved $^{228}$Th and $^{228}$Ra samples were collected by pumping water filtered at 0.8 μm over in-line QMA and Supor filters using McLane in-situ pumps, and then over MnO$_2$ coated acrylic cartridges (Henderson et al. 2013; Maiti et al. 2015). Particulate samples for all Th isotopes were collected via battery-operated McLane in-situ pumps in two size classes: 0.8–51 μm, the small size fraction (SSF) and >51 μm, the large size fraction (LSF). All data from the GEOTRACES GP16 section presented in this paper are available in the 2017 GEOTRACES Intermediate Data Product (Schlitzer et al. 2018). The data is also archived at the Biological and Chemical Oceanography Data Management Office (BCO-DMO).

2.2.2.1 $^{234}$Th

The methods for analyzing GP16 samples for total and particulate $^{234}$Th have been summarized previously (Black et al. 2018). Briefly, 4 L samples for analysis of total $^{234}$Th were spiked with $^{230}$Th as a yield monitor, pre-concentrated by co-precipitation with MnO$_2$, and collected on Whatman quartz microfiber (QMA) filters. Particulate $^{234}$Th samples were
taken in two size fractions using in-situ pumps. The LSF particles were collected onto a pre-filter, and rinsed onto silver filters. SSF particles were filtered onto QMA filters. The activity of $^{234}$Th for both total and particulate samples was determined using anti-coincidence beta counters and corrected for background radioactivity. To compute the radioactive disequilibrium of $^{234}$Th, $^{238}$U was predicted for each sample by the U-salinity relationship of Owens et al. (2011). Dissolved $^{234}$Th is calculated as the difference between the total and particulate pools.

2.2.2.1 $^{230}$Th

The $^{230}$Th data and methods in this paper have been previously published (Pavia et al. 2018). Seawater samples (~5 L) were filtered over 0.45 μm Acropak capsule filters at sea and acidified to pH = 2 using redistilled 6M hydrochloric acid for storage and on-shore analysis. Size-fractionated particulate $^{230}$Th samples were taken using in-situ pumps, with LSF particles collected on a Sefar polyester mesh prefilter, and SSF particles collected on paired 0.8 μm Supor filters. Dissolved samples were spiked with $^{229}$Th, co-precipitated using iron oxyhydroxide, then digested using HF, HNO$_3$, and HClO$_4$. Particulate samples were spiked with $^{230}$Th and dissolved using HNO$_3$ and HClO$_4$, followed by iron co-precipitation and subsequent redissolution. For both dissolved and particulate samples, thorium isotopes were then separated using anion exchange chromatography (BioRad AG1-X8). Concentrations of $^{230}$Th were determined on a Thermo ELEMENT XR single collector inductively-coupled plasma mass spectrometer in peak jumping mode. Dissolved $^{230}$Th data presented here have been corrected for detrital $^{230}$Th present in the dissolved pool from the dissolution of continental material (e.g. Roy-Barman et al. 2009), and in-
growth from $^{234}$U decay during sample storage. The $^{234}$U activity in each sample was computed by multiplying the $^{238}$U-salinity relationship (Owens et al. 2011) by the oceanic $^{234}$U/$^{238}$U activity ratio of 1.1468 (Andersen et al. 2010).

### 2.2.2.3 $^{228}$Th and $^{228}$Ra

Filtered seawater was pumped over MnO$_2$-coated cellulose filters by McLane in-situ pumps to collect dissolved $^{228}$Th and $^{228}$Ra samples. Typically, 1500–1700 L of seawater was filtered at an average flow rate of 6.5 L min$^{-1}$ with an average cartridge collection efficiency of 66 ± 17%. Particulate samples were collected in the SSF on QMA filters via the same in-situ pumps. Full procedures for the analysis of $^{228}$Ra on the GP16 section have been published (Kipp et al. 2018b). The MnO$_2$ cartridges and QMA filters were counted for $^{228}$Th via $^{220}$Rn emanation with the RaDeCC alpha delayed coincidence system (Charette et al. 2015; Maiti et al. 2015; Moore and Arnold 1996). This method detects adsorbed $^{228}$Th capable of releasing $^{220}$Rn; the resulting particulate activity should therefore be considered a lower limit, as there may be additional $^{228}$Th in phases that trap its $^{220}$Rn from being released. For dissolved samples, after RaDeCC analysis, the MnO$_2$-coated cartridges were ashed and gamma counted for $^{234}$Th and $^{226}$Ra on high purity, well-type germanium detectors. The cartridge-based $^{234}$Th and $^{226}$Ra measurements were compared to small-volume (~4 L) beta counting measurements of $^{234}$Th and $^{226}$Ra collected from Niskin bottles hung at the depth of each sample, and the ratio of $^{234}$Th and $^{226}$Ra measured on the small-volume samples to that measured on the MnO$_2$-coated cartridges was used to calculate the collection efficiency of $^{228}$Th and $^{228}$Ra on the cartridges (Maiti et al. 2015).

$^{228}$Ra activities were measured on gamma detectors located underground at the Lab-
oratoire Souterrain de Modane in France and the HADES laboratory in Belgium. The underground location of these laboratories serves to minimize the amount of cosmic radiation reaching the detectors, reducing the detection limits.

2.3 Results

At stations 18 and 20 there is a clear signature of hydrothermal scavenging observed in the profiles of all three thorium isotopes below 2200 m (Figure 2.2). The most distinct signal for the shorter lived $^{234}$Th and $^{228}$Th is enrichment in the particulate phase. In background, non-plume influenced deep waters, particulate $^{234}$Th makes up less than 5% of the total $^{234}$Th, with activities of 1.4–1.8 mBq/kg. In the hydrothermal plume at stations 18 and 20, particulate $^{234}$Th reaches a peak of 32% of the total pool and consistently has activities of 9–12 mBq/kg. Particulate $^{230}$Th increases from background values near 2 μBq/kg to more than 4 μBq/kg, reaching 57% of the total pool. Particulate $^{228}$Th increases from 0.1–0.5 μBq/kg in non-plume waters to 3.5–4.5 μBq/kg within the plume, peaking at 36% of the total $^{228}$Th. At station 21, there is a slight enrichment in particulate $^{234}$Th to 3.97 mBq/kg and in particulate $^{228}$Th to 1.76 μBq/kg. There is little sign of significant excess in or deficit of total $^{234}$Th relative to its parent $^{238}$U. A steady state mass balance model of $^{234}$Th can be used to determine scavenging and removal rates of $^{234}$Th in hydrothermal plumes (Kadko 1996). The mass budget for dissolved $^{234}$Th can be written:

$$\frac{\partial^{234}{\text{Th}}_{\text{diss}}}{\partial t} = \left(^{238}\text{U} - ^{234}\text{Th}_{\text{diss}}\right) \lambda - J_{\text{th}}$$  (2.1)
Figure 2.2: Profiles of at station 18 (top row), station 20 (middle row), and station 21 (bottom row) of thorium isotopes and their parent activities from the GP16 section. Dissolved $^{238}$U, and total, particulate, and dissolved $^{234}$Th are shown in panels A, D, and G. Dissolved, particulate, and total $^{230}$Th are shown in panels B, E, and H. Dissolved $^{228}$Ra, and dissolved, particulate, and total $^{228}$Th are shown in panels C, F, and I. Error bars represent 1-sigma uncertainty, and are smaller than the symbol size where not visible.
where $^{238}\text{U}$ is the dissolved $^{238}\text{U}$ inventory (Bq/m$^2$) in the plume, defined here as the depth interval between 2200 and 3000 m, $^{234}\text{Th}_{\text{diss}}$ is the dissolved $^{234}\text{Th}$ inventory (Bq/m$^2$) in the plume, $\lambda$ is the decay constant of $^{234}\text{Th}$ in yr$^{-1}$, and $J_{\text{Th}}$ is the net rate at which dissolved $^{234}\text{Th}$ is adsorbed onto particles in Bq m$^{-2}$ yr$^{-1}$. Assuming steady state, we can solve for $J_{\text{Th}}$, then the net adsorption rate constant of $^{234}\text{Th}$ in the plume ($k_1$, in units yr$^{-1}$) by dividing the scavenging rate by the dissolved $^{234}\text{Th}$ inventory:

$$k_1 = \frac{J_{\text{Th}}}{^{234}\text{Th}_{\text{diss}}} \quad (2.2)$$

At station 18, we derive $J_{\text{Th}} = 106 \pm 16$ Bq m$^{-2}$ day$^{-1}$ and $k_1 = 2.99 \pm 0.47$ yr$^{-1}$. At station 20, we find $J_{\text{Th}} = 147 \pm 31$ Bq m$^{-2}$ day$^{-1}$ and $k_1 = 2.32 \pm 0.51$ yr$^{-1}$. At station 21, $J_{\text{Th}}$ and $k_1$ decrease to $35.5 \pm 17$ Bq m$^{-2}$ day$^{-1}$ and $1.21 \pm 0.58$ yr$^{-1}$ respectively. Our estimates of $J_{\text{Th}}$ are comparable to previous values of 152 Bq m$^{-2}$ day$^{-1}$ found by Owens et al. (2015) at the Mid-Atlantic Ridge and 81.6–202 Bq m$^{-2}$ day$^{-1}$ found by Kadko et al. (1994) at the Juan de Fuca Ridge. Unlike $^{234}\text{Th}$, there is a large deficit of total $^{230}\text{Th}$ in the hydrothermal plume at stations 18–21 relative to the concentration profiles expected for removal by reversible scavenging. Reversible scavenging should drive dissolved, particulate, and total $^{230}\text{Th}$ activities to linearly increase with depth throughout the water column (Bacon and Anderson 1982). Above the hydrothermal plume this is the case along GP16 (Pavia et al. 2018); however, below 2200 m at stations 18–21, total $^{230}\text{Th}$ sharply declines from 15–17 μBq/kg to less than 5 μBq/kg (Figure 2.2). A similar signal is seen in the dissolved phase, and the depletion of both total and dissolved $^{230}\text{Th}$ in the hydrothermal plume is roughly similar between the three stations. Whereas the imprint of hydrother-
Figure 2.3: Fractions of total particulate (sum of LSF and SSF size fractions) $^{230}$Th (blue dots), $^{234}$Th (red upside-down triangles), particulate MnO$_2$ (green diamonds), and particulate Fe(OH)$_3$ (black triangles) found in the large size fraction (>51 μm) from GP16 stations 18 (A), 20 (B), and 21 (C). Fe(OH)$_3$ and MnO$_2$ data from Lam et al. (2018). 1-Sigma uncertainties are shown for $^{234}$Th and $^{230}$Th and are smaller than the symbol size where not visible.

Normal scavenging signals on $^{234}$Th essentially disappeared by station 21, roughly 250 km from the EPR, the hydrothermal depletion of dissolved and total $^{230}$Th and enrichment of particulate $^{230}$Th extends over 4000 km from the ridge axis (Pavia et al. 2018).

2.4 Discussion

2.4.1 Size Partitioning of $^{234}$Th and $^{230}$Th

The isotopes of thorium are expected to have identical chemical scavenging behavior. Differences in observed scavenging intensities of the different isotopes can therefore be attributed to the different timescales over which they integrate, which are related to their half-lives. One of the key variables in determining the scavenging rates and sinking fluxes of particles is their size (Burd and Jackson 2009). Smaller particles typically have a larger surface area to volume ratio, allowing for greater adsorption per unit mass of particles.
Figure 2.4: Scatter plots of fLSF (fraction of total particulate thorium found in >51 μm particles, see Equation 2.3) for $^{234}$Th and $^{230}$Th. Samples not in the hydrothermal plume (2200–3000 m) at stations 18, 20, and 21 are shown as dots. Samples within the hydrothermal plume as stations 18–21 are shown as open triangles. The dashed line shows the 1:1 line that would be expected if $^{234}$Th and $^{230}$Th were partitioned equally into the >51 μm size fraction. The solid line shows the best-fit linear slope of 0.77, indicating that $^{230}$Th is preferentially incorporated into >51 μm particles in non-plume samples.

(Honeyman and Santschi 1989), while larger particles are exported faster by gravitational settling (Burd and Jackson 2009). Measuring thorium isotopes with varying half lives in particles of different size classes can be used to constrain the aggregation of small particles, with large surface area to mass ratios, into large particles that settle more rapidly.

On the GP16 section, particulate $^{234}$Th measurements were made on both the LSF and SSF throughout the water column. Particulate $^{230}$Th was mostly measured in the SSF, but
there are 44 LSF measurements, including 17 in the hydrothermal plume at stations 18–21 that permit comparison with $^{234}$Th. $^{228}$Th was only measured in the SSF, so we can only compare the size partitioning of $^{234}$Th and $^{230}$Th. To do this, we use the fraction of thorium activity found in the large size fraction relative to the total particulate activity (Lee et al. 2018):

$$f_{\text{LSF}} = \frac{[\text{pTh}]_{\text{LSF}}}{[\text{pTh}]_{\text{LSF}} + [\text{pTh}]_{\text{SSF}}} \quad (2.3)$$

where $[\text{pTh}]$ is the particulate activity of thorium. For the data outside the hydrothermal plume, a slightly higher fraction of particulate $^{230}$Th is found in the large size fraction that $^{234}$Th (Figure 2.3). Linear regression of $f_{\text{LSF}}$ of $^{234}$Th against $f_{\text{LSF}}$ of $^{230}$Th from the entire GP16 section ($n = 44$ samples) reveals an intercept of 0, but a slope of $0.77 \pm 0.09$ ($r^2 = 0.63$), indicating consistently higher $f_{\text{LSF}}$ of $^{230}$Th (Figure 2.4). This could be explained by the kinetics of adsorption and desorption being more rapid than those of aggregation-disaggregation, as $^{234}$Th would have decreased via radioactive decay to lower activities during the aggregation of the SSF into large particles much more so than $^{230}$Th, leaving more $^{230}$Th in the LSF than $^{234}$Th. Since there is limited sampling of $^{230}$Th and $^{228}$Th in the >51 μm size fraction, inverse models of particle cycling must assume identical size partitioning of the different thorium isotopes to calculate the bulk (SSF + LSF) particulate activities of these isotopes (Lerner et al. 2016, 2017). More measurements of $^{230}$Th and $^{228}$Th in the LSF would be highly beneficial for further constraining the differential size partitioning of thorium isotopes and its effect on models of particle cycling.

At stations 18–21, there are 17 measurements of particulate $^{230}$Th in the LSF in the depth range of the hydrothermal plume. The slope of the regression between $f_{\text{LSF}}$ of $^{234}$Th...
against fLSF of $^{230}$Th for these samples is $0.9 \pm 0.24$ – much closer to the expected 1:1 line than for samples collected outside the plume (Figure 2.4). While the difference in slopes is not statistically significant, these results are still suggestive that particle aggregation at station 20, and in general the near-axis hydrothermal plume, is more rapid than in the typical deep ocean. Rapid particle aggregation is consistent with the enrichment of fLSF for pFe, pMn, and bulk suspended particulate matter (SPM) in the hydrothermal plume relative to samples taken above the plume at stations 18 and 20 (Lee et al. 2018). The similar size partitioning of $^{234}$Th and $^{230}$Th within the plume also indicates that the greater depletion of total $^{230}$Th than total $^{234}$Th in the plume cannot be due to differential incorporation of $^{230}$Th into faster sinking particles.

2.4.2 Scavenging Intensity of Thorium

The paradigm for understanding $^{230}$Th cycling in the ocean is reversible scavenging, whereby thorium reversibly exchanges between the dissolved phase and a small, slow-sinking particulate phase, resulting in the linear increase of both dissolved and particulate $^{230}$Th activities with depth (Bacon and Anderson 1982). In this model, the ratio of particulate thorium activity ($A_p$) to dissolved thorium activity ($A_d$), or $K_{Th}$, is a function of the relative rates of dissolved thorium adsorption onto particles ($k_1$), desorption and remineralization of thorium from particles into solution ($k_{-1}$), and the radioactive decay constant ($\lambda$):

$$K_{Th} = \frac{A_p}{A_d} = \frac{k_1}{\lambda + k_{-1}}$$

(2.4)
Figure 2.5: Particulate (SSF only) to dissolved ratios ($K$) of $^{228}$Th (green diamonds), $^{230}$Th (blue circles), and $^{234}$Th (red upside-down triangles) at GP16 stations 18 (A), 20 (B), and 21 (C). Uncertainties are 1-sigma and are smaller than the symbol size where not visible.

In the reversible scavenging model, variations in $K$ for a given isotope would be due to changes in the relative rates of adsorption and desorption. For $^{230}$Th, the decay constant is negligible, so Equation 2.4 can be simplified to $K = k_1/k_{-1}$. Because this conceptualization of $K$ does not include sinking losses of particulate thorium, we compute $K$ using only the ratio of small particulate thorium activity to dissolved thorium activity. We find that $K$ values increase for all of the thorium isotopes in the hydrothermal plume (Figure 2.5). $K$ is consistently higher for $^{230}$Th than for the two shorter-lived isotopes, which is reasonable given that the decay constants for $^{230}$Th, $^{228}$Th, and $^{234}$Th are $9.1 \times 10^{-6}$ yr$^{-1}$, 0.36 yr$^{-1}$, and 10 yr$^{-1}$, respectively. Thus, if $k_1$ and $k_{-1}$ are the same for all the thorium isotopes, we would expect $K$ to be largest for $^{230}$Th, and smallest for $^{234}$Th. However, the $K$ values of $^{234}$Th and $^{228}$Th are similar to each other both above and within the hydrothermal plume.

For average deep ocean values of $k_1 = 0.71$ yr$^{-1}$, and $k_{-1} = 2.7$ yr$^{-1}$ (Lerner et al. 2017), we would expect to observe $K$ values of 0.27 for $^{230}$Th, 0.23 for $^{228}$Th, and 0.05 for $^{234}$Th. We note that the average values of Lerner et al. (2017) are for the deep North Atlantic, and may be somewhat different in the South Pacific. These estimates are still close to observations.
Figure 2.6: Adsorption (A) and desorption (B) rate constants (yr$^{-1}$) for thorium cycling on the GP16 section, as well as the desorption/adsorption rate constant ratio (C). Rate constants are calculated by plugging measured K values for both $^{234}$Th and $^{230}$Th into Equation 2.4 (Bacon and Anderson 1982).

for $^{230}$Th and $^{234}$Th, but the observed K values for $^{228}$Th are much smaller than predicted, closer to those of $^{234}$Th (Figure 2.5). This may be an artifact of the measurement method, which can only detect surface adsorbed $^{228}$Th. If there is additional $^{228}$Th inside particles, perhaps as the result of metal oxide co-precipitation during hydrothermal plume particle formation, this would result in higher K values for $^{228}$Th.

We can use Equation 2.4 to calculate $k_1$ and $k_{-1}$ values at each station using the measured K values for both $^{230}$Th and $^{234}$Th (Bacon and Anderson, 1982). We find increases in both adsorption and desorption rate constants from 2400-2500 m at stations 18 and 20 (Figure 2.6), similar to increases in both rate constants found at the TAG hydrothermal vent site in the North Atlantic (Lerner et al. 2017). However, below 2500 m, the depth of this sharp increase, adsorption and desorption rates rapidly decline, the desorption rates falling below values above the plume, and the ratio of $k_{-1}/k_1$ reaches a minimum (Figure 2.6).
Reversible scavenging assumes that suspended deep ocean particles are at a steady state between adsorption of Th and desorption plus decay of Th. However, Bacon and Anderson (1982) also propose a hybrid model where the adsorption of Th is balanced by decay, desorption, and incorporation of Th into a fast sinking flux, the third process accomplished by the aggregation of small particles into large, faster sinking particles.

At stations 18 and 20, both bulk (SSF + LSF) and LSF SPM within the plume are strongly elevated over background levels outside the plume (Lam et al. 2018), generating conditions where particle sinking could be rapid enough to affect the steady state balance of thorium isotopes. Under these conditions, the ratio of particulate to dissolved thorium activity would be described as:

\[ K_{\text{Th}} = \frac{k_1}{\lambda + k_{-1} + k_2} \] (2.5)

where the new term \( k_2 \) is the rate constant for the rapid removal of small particulate Th by aggregation into rapidly settling large particles. Since we compute K only using 0.8–51 μm particles, the \( k_2 \) term is equivalent to an aggregation rate for the conversion of 0.8–51 μm particles into >51 μm particles. Given the faster particle aggregation inferred from the similar size partitioning of \(^{234}\text{Th}\) and \(^{230}\text{Th}\) in the hydrothermal plume (Section 2.4.1), it is likely that particle aggregation is a significant loss term in the budget of small particulate thorium. Thus, \( k_{-1} \) values we derived using Equation 2.4 are in reality a combination of the desorption rate constant and the particle aggregation rate constant. This would imply even lower values for the desorption rate constant than what were previously inferred, especially at stations 18 and 20 where fLSF of particulate Th isotopes is highest.

The controls on Th desorption rate are poorly understood. Values we compute for \( k_{-1} \)
on GP16 are lower than average values in the deep North Atlantic ocean (e.g. Lerner et al. 2017), especially when the additional effect of particle aggregation is considered. We argue that lower desorption rates are a consequence of a portion of dissolved Th being scavenged irreversibly. Thousands of kilometers west of Station 21, where most of the high mass of pMn has been removed, K values for \(^{230}\)Th and \(^{231}\)Pa remain anomalously high and Th/Pa fractionation factors are anomalously low with respect to the background deep ocean, and close to the endmember values of particulate manganese and iron scavenging (Pavia et al. 2018). One possibility is that Th simply binds to some Fe and Mn particles irreversibly. Another hypothesis is that the production of new Mn and Fe surfaces on particles creates a physical barrier between seawater and solutes already bound to the particle, preventing desorption back into solution and resulting in the irreversible scavenging of Th. Additional research is required to discriminate between these two possibilities.

### 2.4.3 Variable Depletion Among the Th Isotopes

Measurements of the three thorium isotopes can be used to study the kinetics of scavenging in the early history of the hydrothermal plume. Total \(^{230}\)Th is highly depleted in the plume relative to reversible scavenging, while total \(^{234}\)Th is nearly in secular equilibrium with its parent \(^{238}\)U. This difference informs us about the time scale for scavenging and removal.

We can quantify the percent depletion of any thorium isotope at a given depth by the
following equation (Lopez et al. 2015; Pavia et al. 2018):

\[
\text{Percent Depletion} = \frac{A_{\text{pred}} - A_{\text{obs}}}{A_{\text{pred}}} \times 100
\]  \hspace{1cm} (2.6)

where \(A_{\text{pred}}\) is the predicted total (dissolved + bulk particulate) activity of a Th isotopes, and \(A_{\text{obs}}\) is the observed total activity. Given the need to use total activities, and the lack of \(^{230}\text{Th}\) and \(^{228}\text{Th}\) measurements in the large size fraction for every sample, we multiply SSF activities of \(^{230}\text{Th}\) (where there are no measurements in the LSF) and \(^{228}\text{Th}\) by the LSF/SSF activity ratio observed for \(^{234}\text{Th}\) for a given sample to estimate the LSF contribution to the total \(^{228}\text{Th}\) and \(^{230}\text{Th}\) for that sample.

For \(^{234}\text{Th}\), the predicted activity is that of its parent isotope \(^{238}\text{U}\) (secular equilibrium). For \(^{230}\text{Th}\), the predicted activity is derived by extrapolating the increase in activity with depth above the hydrothermal plume into the observed depths within the hydrothermal plume, as expected from reversible scavenging (Bacon and Anderson 1982; Lopez et al. 2015; Pavia et al. 2018).

For \(^{228}\text{Th}\), the predicted activity is more complicated. Since the half-life of \(^{228}\text{Th}\) is only slightly shorter than that of its parent \(^{228}\text{Ra}\), in a closed system \(^{228}\text{Th}\) will approach a transient equilibrium with \(^{228}\text{Ra}\) where \(^{228}\text{Th}/^{228}\text{Ra}\) activity ratios reach 1.5 (e.g. Turekian et al. 1975). This behavior has been modeled in studies of shelf-basin exchange and scavenging dynamics (Kipp et al. 2018a; Rutgers van der Loeff et al. 2012; Rutgers van der Loeff et al. 2018). We adapt these models for use in the GP16 hydrothermal plume. For a purely advective system, once hydrothermal supply of \(^{228}\text{Ra}\) has ceased, \(^{228}\text{Ra}\) activities will change
only as a function of radioactive decay over time (t):

\[ {^{228}\text{Ra}(t)} = {^{228}\text{Ra}_0} e^{-\lambda_{^{228}\text{Ra}} t} \]  \hspace{1cm} (2.7)

In this and the following equation, the subscript \( \_0 \) indicates initial activity at the time when the hydrothermal plume leaves the ridge. The activity of \(^{228}\text{Th}\) at time \( t \) is a function of ingrowth, decay, and scavenging (Kipp et al. 2018a; Rutgers van der Loeff et al. 2012; Rutgers van der Loeff et al. 2018):

\[ {^{228}\text{Th}(t)} = {^{228}\text{Th}_0} e^{-(\lambda_{^{228}\text{Th}} + \lambda_s) t} + \left( \frac{\lambda_{^{228}\text{Th}}}{\lambda_{^{228}\text{Th}} + \lambda_s - \lambda_{^{228}\text{Ra}}} \right) \times \left( {^{228}\text{Ra}_0} e^{-\lambda_{^{228}\text{Ra}} t} - e^{-(\lambda_{^{228}\text{Th}} + \lambda_s) t} \right) \]  \hspace{1cm} (2.8)

where \( \lambda_{^{228}\text{Th}} \) and \( \lambda_{^{228}\text{Ra}} \) are the decay constants of \(^{228}\text{Th}\) and \(^{228}\text{Ra}\), and \( \lambda_s \) is the \(^{228}\text{Th}\) scavenging rate constant. This model neglects the impacts of lateral and vertical mixing on \(^{228}\text{Th}\) and \(^{228}\text{Ra}\), and requires knowledge of the initial \(^{228}\text{Th}\) and \(^{228}\text{Ra}\) activities at the time the plume advects away from the ridge axis. We use the \(^{228}\text{Ra}\) and \(^{228}\text{Th}\) activities at station 18 as the initial values to predict \(^{228}\text{Th}/^{228}\text{Ra}\) ratios at stations 20 and 21. Plume ages (t) at stations 18 and 20 were determined using a wide range of off-axis flow velocities in the hydrothermal plume of 0.1–0.5 cm/s based on dilution-corrected \(^{227}\text{Ac}\) decay (Hammond et al. 2016; Lupton and Jenkins 2017), neutrally buoyant floats (Lupton and Jenkins 2017), and inverse modeling (Faure and Speer 2012; Hautala and Riser 1993). These flow velocities, multiplied by the distances of stations 20 (81 km) and 21 (243 km) from the ridge, yield plume ages of 0.5–2.6 yr at station 20, and 1.5–7.7 yr at station 21.

The best-fit off-axis scavenging rate for the measured \(^{228}\text{Th}/^{228}\text{Ra}\) ratios at stations 20
Figure 2.7: Observed and modeled total (dissolved + particulate) $^{228}\text{Th}/^{228}\text{Ra}$ activity ratios in the hydrothermal plume for a range of initial $^{228}\text{Th}$ and $^{228}\text{Ra}$ activities. Panel A) shows the modeled evolution of $^{228}\text{Th}/^{228}\text{Ra}$ using the mean values of $^{228}\text{Ra}$ and $^{228}\text{Th}$ below 2400 m at station 18 as initial activities in Equations 2.7 and 2.8. Panel B) shows the same model, but with the lower bound of the $^{228}\text{Th}/^{228}\text{Ra}$ ratio at station 18 as the initial activities, and Panel C) shows the same model with the upper bound of $^{228}\text{Th}/^{228}\text{Ra}$ at station 18 as the initial activities. The solid lines represent the modeled $^{228}\text{Th}/^{228}\text{Ra}$ activity ratio in for a range of scavenging rate constants: black is the no scavenging scenario ($\lambda_s = 0$ yr$^{-1}$ in Equation 2.8), red is $\lambda_s = 0.1$ yr$^{-1}$, green is $\lambda_s = 0.15$ yr$^{-1}$, and blue is $\lambda_s = 0.2$ yr$^{-1}$. Mean observed total $^{228}\text{Th}/^{228}\text{Ra}$ activity ratios within the hydrothermal plume at stations 18, 20, and 21 and their 1-sigma uncertainties are shown as diamonds, circles, and squares, respectively. Plume ages and their uncertainties at stations 20 and 21 are derived from $^{227}\text{Ac}$ measurements and physical oceanographic estimates of flow velocities (see Section 2.4.3).

and 21 is 0.15 yr$^{-1}$ (Figure 2.7). The mean ratio of $^{228}\text{Th}/^{228}\text{Ra}$ activities below 2400 m at station 18 is 0.9. The best-fit scavenging rate of 0.15 is relatively insensitive to the initial $^{228}\text{Th}/^{228}\text{Ra}$ ratio, consistent with the upper and lower error bounds of the $^{228}\text{Th}/^{228}\text{Ra}$ ratio at station 18 – varying only by ~0.05 yr$^{-1}$ for the range of initial $^{228}\text{Th}/^{228}\text{Ra}$ ratios at station 18 (Figures 2.7b and 2.7c). Since the $^{228}\text{Th}/^{228}\text{Ra}$ ratios at stations 18–21 are relatively invariant, and the scavenging rate of 0.15 yr$^{-1}$ results in a nearly constant $^{228}\text{Th}/^{228}\text{Ra}$ ratio over time, our results are also insensitive to uncertainties in the plume ages. While we do not take mixing into account, the effect of lateral mixing on the $^{228}\text{Th}/^{228}\text{Ra}$ ratios should also be minimal, since $^{228}\text{Th}$ and $^{228}\text{Ra}$ activities are both a factor of 2–3 higher in
Figure 2.8: Percent removal for total pools of $^{234}$Th (red upside-down triangles), $^{228}$Th (green diamonds), and $^{230}$Th (blue circles) at stations 18 (A), 20 (B), and 21 (C). Uncertainties shown are 1-sigma. Station 18 is used to constrain the initial conditions for the $^{228}$Th–$^{228}$Ra pair, so there is no percent removal value for $^{228}$Th shown in (A).

the hydrothermal plume than in overlying waters, which we take to be representative of background, non-plume waters (Figure 2.2c). The off-axis hydrothermal Th scavenging rate constant of $0.15 \pm 0.05$ yr$^{-1}$ will be useful for future studies of off-axis scavenging dynamics. We can use the no scavenging scenario (solid black lines in Figure 2.7, $\lambda_s = 0$ in Equation 2.8) to determine the percent depletion of $^{228}$Th at stations 20 and 21, but not station 18, since we initiate the model using the $^{228}$Th/$^{228}$Ra ratios from station 18. In Equation 2.6, $A_{\text{pred}}$ is the $^{228}$Th/$^{228}$Ra ratio of the no scavenging scenario (dashed line in Figure 2.7c) at the age of the plume at a given station, and $A_{\text{obs}}$ is the averaged observed $^{228}$Th/$^{228}$Ra ratio at that station. The percent depletion is thus averaged within the plume, and we display the average value at 2500 m in Figure 2.8.

Depletion of total $^{230}$Th in the hydrothermal plume relative to that predicted by extrapolating trends above 2000 m reaches a maximum of 70% at stations 18–20 (Figure 2.8). At those stations, total $^{234}$Th is only depleted a maximum of 8%. Depletion of total $^{228}$Th is $28 \pm 12\%$ at station 20 and $31 \pm 14\%$ at station 21. Scavenging occurring over 100 days
in the past would have a negligible lasting imprint on $^{234}$Th, but $^{230}$Th and $^{228}$Th would largely retain the signal of scavenging. Greater depletion of $^{230}$Th and $^{228}$Th than $^{234}$Th at those stations could indicate that the majority of the Th was scavenged and removed from seawater over 100 days prior to sampling, long enough for $^{234}$Th to have nearly returned to its predicted value of secular equilibrium.

If this early scavenging history were true, and the scavenging was the result of the most recent input of hydrothermal materials, then we might expect the scavenging signals of the three thorium isotopes to be coherent at station 18, which was sampled directly above the EPR, though not necessarily above an active vent. Station 18 had measurable $^{223}$Ra ($t_{1/2} = 11.4$ days), meaning that there had been a recent input of hydrothermal fluids. However, there was no hydrothermal $^{224}$Ra ($t_{1/2} = 3.66$ days), which is enriched in high-temperature vent fluids (Kipp et al. 2018b), indicating that the plume was at least 18 days (five $^{224}$Ra half-lives) old. Using a range of $^{223}$Ra/$^{226}$Ra ratios observed in vent fluids, Kipp et al. (2018b) constrained the age of the hydrothermal plume at Station 18 to be 24–32 days. However, it is possible that hydrothermal activity >50 days in the past could have injected additional $^{226}$Ra, which would decrease the apparent age of the plume since any additional $^{223}$Ra injected would have decayed away. Thus we suggest that a more appropriate age range of the hydrothermal plume at station 18 is 18–32 days. Future surveys of Ra injection along the EPR may be able to confirm where and when additional hydrothermal $^{226}$Ra is added as waters flow northward above the ridge.

At station 18, the depletion of $^{230}$Th reaches 70%, while the maximum depletion of $^{234}$Th is 8%. Given that the 18–32 day age of the plume is similar to the half-life of $^{234}$Th, if the two Th isotopes had been removed to the same degree at the EPR crest 18–32 days prior
Figure 2.9: Modeled $^{234}$Th depletion (y-axis) as a function of elapsed time after a 70% depletion (maximum observed $^{230}$Th depletion relative to reversible scavenging) of $^{234}$Th (x-axis). The dashed line corresponds to the predicted depletion of $^{234}$Th if 70% scavenging had occurred 32 days previously, the upper limit for the age of the plume at Station 18. The dotted line marks the time necessary to have elapsed for an 8% depletion of $^{234}$Th to be observed at station 18.

to sample collection, then a far greater depletion of $^{234}$Th should be observed. Below, we model the time evolution of Th isotopes following a scavenging event to specifically test whether our data are consistent with a single recent scavenging event being responsible for the 8% depletion of total $^{234}$Th and 70% depletion of $^{230}$Th at station 18.

The mass balance of a radioactive daughter isotope (denoted here $N_2$, in atoms) of a given parent ($N_1$, in atoms) following scavenging removal can be written from the Bate-
man equations for radioactive decay as follows:

\[
\frac{dN_2}{dt} = \lambda_1 N_1^0 e^{-\lambda_1 t} - \lambda_2 N_2 \tag{2.9}
\]

where \( \lambda \) is the decay constant of the isotope, \( N_0 \) indicates the initial atoms of the parent isotope present, and \( t \) is time elapsed since a scavenging event early in the history of the hydrothermal plume. This equation can be solved for the number of \( N_2 \) daughter atoms present at time \( t \):

\[
N_2(t) = \frac{\lambda_1}{\lambda_2 - \lambda_1} N_1^0 (e^{-\lambda_1 t} - e^{-\lambda_2 t}) + N_2^0 e^{-\lambda_2 t} \tag{2.10}
\]

The first term on the right side of the Equation 2.10 is the number of \( N_2 \) atoms present that have ingrown from its parent \( N_1 \), but have not yet undergone radioactive decay. The second term on the right side of the equation is the loss by radioactive decay of the daughter nuclide initially present immediately after the scavenging event. We can use this model to assess the depletion that ought to be observed if \(^{234}\text{Th} \) experienced the same 70% depletion as \(^{230}\text{Th} \) at the upper age limit of the plume age (32 days) derived from \(^{223}\text{Ra}/^{226}\text{Ra} \) dating – the most conservative possible condition, allowing the most time for \(^{234}\text{Th} \) ingrowth from U decay. If \(^{234}\text{Th} \) was 70% depleted 32 days before sampling, there should have been a 30% deficit in \(^{234}\text{Th} \) observed at station 18 (dashed line in Figure 2.9), far greater than the observed maximum of 8% depletion.

If we assume that 70% depletion of \(^{234}\text{Th} \) did occur and that the plume age is an unknown variable, then we can solve for the minimum amount of time that must have
elapsed for 8% depletion to be observed at station 18. For 8% depletion to be measured at station 18, 70% removal of $^{234}$Th would have to have happened 75 days prior to sampling (dotted line in Figure 2.9). The observed $^{223}$Ra/$^{226}$Ra ratio at station 18 of 0.011 and a 75 day old plume would require a vent fluid $^{223}$Ra/$^{226}$Ra activity of 1.09, which is both 2–3 times larger than the maximum $^{223}$Ra/$^{226}$Ra ratios ever measured in vent fluids, and over an order of magnitude larger than the average vent fluid $^{223}$Ra/$^{226}$Ra ratio (Kipp et al. 2018b). It is also an order of magnitude higher than $^{231}$Pa/$^{226}$Ra activity ratios measured in basalts from the EPR, which, at steady state, set the $^{223}$Ra/$^{226}$Ra ratios of vent fluids (Bourdon et al. 2000; Lundstrom et al. 1999; Sims et al. 2002). The decoupling of $^{234}$Th depletion and $^{230}$Th depletion could be explained if $^{230}$Th had preexisting depletion due to scavenging that had occurred before the most recent injection of hydrothermal material prior to sampling at station 18.

Finally, we rearrange Equation 2.10 to solve for the maximum initial removal of $^{234}$Th ($N^0_2$) in the early history of the hydrothermal plume:

$$N^0_2 = \frac{N_2(t) - \frac{\lambda_1}{\lambda_2 - \lambda_1} N^0_1 \left(e^{-\lambda_1 t} - e^{-\lambda_2 t}\right)}{e^{-\lambda_2 t}}$$

(2.11)

We find that an 18–32 day plume age and maximum observed depletion of $^{234}$Th of 8% at station 18 would require the instantaneous Th removal of 14–20% since the water mass encountered the vent source of the hydrothermal plume, much less than the 70% observed depletion of $^{230}$Th at station 18. Given the enrichment of particulate $^{234}$Th at station 18 but lack of total depletion, it is likely that particle aggregation and sinking occurs on timescales greater than the half-life of $^{234}$Th, so instantaneous 14–20% depletion of $^{234}$Th
at a vent is an endmember scenario rather than a requirement of our model. Regardless,
we have shown that the 70% depletion of $^{230}$Th cannot be explained by a single recent scav-
enging event, indicating that $^{230}$Th has an inherited scavenging signal, most reasonably
from hydrothermal activity preceding the most recent scavenging event.

Float trajectories and modeling studies suggest topographically steered equatorward
flow extending hundreds of meters above the EPR ridge axis from 40°S to 10°S, with ve-
locities of 0.2–0.5 cm/s (Hautala and Riser 1993; Zilberman et al. 2017). This flow passes
across a number of active high-temperature hydrothermal vents just south of our study
area (Figure 2.1). Previous surveys documented particularly intense hydrothermal activ-
ity between 17°S–19°S, with Fe- and Mn-rich particle-laden plumes in the water column
(Feely et al. 1996; Urabe et al. 1995). Resing et al. (2015) suggested that the dFe and dMn
enrichment in the GP16 plume at station 20 and westward was from these 17°S–19°S vent
fields. Jenkins et al. (2018) suggested that the $^3$He in the GP16 plume may have been
sourced from further south as well, since the $^3$He and $^4$He were correlated with a slope of
9.04 ± 0.24 R/R$_a$ ($^3$He/$^4$He ratio relative to the atmospheric ratio), higher than the typical
MORB value of 8 R/R$_a$, and consistent with high $^3$He/$^4$He of 9–11 R/R$_a$ in EPR basalts at
17°S (Kurz et al. 2005). We hypothesize that much of the 70% depletion of $^{230}$Th observed
in the GP16 hydrothermal plume is due to scavenging in the particle-rich plumes of this
17°S–19°S region, which then veered west towards stations 20 and 21 (dashed white arrow
in Figure 2.1).

If the $^{230}$Th removal rates were greater than the integrated production rate from U
decay in the overlying water column, it would require a lateral diffusive source of $^{230}$Th,
making this portion of the EPR a boundary sink for $^{230}$Th, and potentially biasing the
near- and off-axis application of sedimentary \(^{230}\text{Th}\)-normalization for determining mass accumulation rates (e.g. Bacon 1984; Francois et al. 2004) in the South Pacific at these latitudes. More research is required to determine the effect of hydrothermal activity on sedimentary \(^{230}\text{Th}\) burial rates.

### 2.5 Conclusions

Combined measurements of dissolved and particulate \(^{234}\text{Th},^{230}\text{Th},\) and \(^{228}\text{Th}\) allowed us to better understand the kinetics of hydrothermal plume particle dynamics and scavenging in the South Pacific Ocean. The size partitioning of \(^{234}\text{Th}\) and \(^{230}\text{Th}\) between \(>51\ \mu\text{m}\) and \(0.8–51\ \mu\text{m}\) particles was more closely coupled in the hydrothermal plume than for typical waters from the rest of the section, indicating that particle aggregation was occurring much more rapidly in the plume. By determining adsorption and desorption rate constants for thorium, in combination with the finding of rapid particle aggregation, we hypothesize that hydrothermal scavenging is partially irreversible.

Modeling the evolution of \(^{228}\text{Th}/^{228}\text{Ra}\) ratios revealed an off-axis hydrothermal Th scavenging rate of \(0.15\ \text{yr}^{-1}\). We found variable removal among the three Th isotopes in the near-axis plume, with \(^{230}\text{Th}\) the most depleted, followed by \(^{228}\text{Th}\), then \(^{234}\text{Th}\). The large degree of \(^{230}\text{Th}\) removal is inconsistent with a single local scavenging event, and is more likely due to progressive scavenging in the region of intense hydrothermal activity from \(17^\circ\text{S}\) to \(19^\circ\text{S}\).

These results illustrate the complexity of interpreting the GP16 hydrothermal plume as being solely a local phenomenon. The time information provided by the radioactivity of
the thorium isotopes shows that the scavenging signals observed in the GP16 section are a result of hydrothermal activity further south on the EPR. Future studies combining data from multiple radiogenic thorium isotopes in this manner will be useful for understanding the time dynamics from other parts of the GP16 section, such as the upper water column, the continental shelf, and benthic nepheloid layers.

Acknowledgements

This work was supported by the U.S. National Science Foundation (OCE-1233688 to LDEO, OCE-1233903 to UMN), OCE-1232669 to WHOI, OCE-1231211 to USC) and an NSF Graduate Research Fellowship to F.J.P. (DGE-16-44869). We thank the captain, crew, and scientists aboard the R/V Thomas G. Thompson. Constructive comments from three anonymous reviewers greatly improved the quality of this manuscript. We are grateful to John Lupton for sharing Helios float trajectories, Ken Buesseler for overseeing the collection of the $^{234}$Th data, and to Phoebe Lam and Kassandra Costa for helpful discussions.
Chapter 3

Shallow particulate organic carbon regeneration in the South Pacific Ocean

Abstract

Particulate organic carbon (POC) produced in the surface ocean sinks through the water column and is respired at depth, acting as a primary vector sequestering carbon in the abyssal ocean. Atmospheric carbon dioxide levels are sensitive to the length (depth) scale over which respiration converts POC back to inorganic carbon, because shallower waters exchange with the atmosphere more rapidly than deeper ones. However, estimates of this carbon regeneration length scale and its spatiotemporal variability are limited, hindering the ability to characterize its sensitivity to environmental conditions. Here, we present a zonal section of POC fluxes at high vertical and spatial resolution from the GEOTRACES GP16 transect in the eastern tropical South Pacific, based on normalization to the radio-
genic thorium isotope $^{230}$Th. We find shallower carbon regeneration length scales than previous estimates for the oligotrophic South Pacific gyre, indicating less efficient carbon transfer to the deep ocean. Carbon regeneration is strongly inhibited within suboxic waters near the Peru coast. Canonical Martin curve power laws inadequately capture POC flux profiles at suboxic stations. We instead fit these profiles using an exponential function with flux preserved at depth, finding shallow regeneration but high POC sequestration below 1,000 m. Both regeneration length scales and POC flux at depth closely track the depths at which oxygen concentrations approach zero. Our findings imply that climate warming will result in reduced ocean carbon storage due to expanding oligotrophic gyres, but opposing effects on ocean carbon storage from expanding suboxic waters will require modeling and future work to disentangle.

### 3.1 Introduction

The oceanic biological pump encompasses a series of processes by which phytoplankton at the sea surface photosynthetically fix carbon dioxide (CO$_2$) to form particulate organic carbon (POC), a portion of which is exported from the upper ocean and sinks to depth, where it is regenerated by microbial respiration (De La Rocha and Passow 2014; Hain et al. 2014). The first two components of the biological pump, primary production and export of POC from the upper ocean, have been sufficiently characterized to enable their parametrization in terms of variables that can be measured by satellites, allowing for comprehensive estimates of their global rates and spatiotemporal variability (Behrenfeld et al. 2001; Behrenfeld and Falkowski 1997; Henson et al. 2011; Siegel et al. 2014). However,
the fate of exported POC upon sinking into the ocean interior has proved to be an elusive oceanographic target. Because the time scale that waters are sequestered from the atmosphere increases with depth, the length scale over which POC regeneration occurs exerts a strong control on oceanic carbon storage and atmospheric CO$_2$ levels (Kwon et al. 2009). Consequently, assessing how environmental conditions influence POC regeneration length scales provides critical insights that can be incorporated into ocean carbon cycle models to improve projections of future oceanic CO$_2$ uptake, including the response to global warming.

Historical estimates of carbon regeneration in the ocean interior have come from POC flux profiles generated either by compilations of sediment traps (Martin et al. 1987); by individual free-floating sediment trap profiles, typically with three to six depths in the upper 500 m (Buesseler et al. 2007; Marsay et al. 2015); or by combining $^{234}$Th-based euphotic zone POC fluxes with those from bottom-moored sediment traps below 1,500 m (Guidi et al. 2015; Henson et al. 2012). POC regeneration length scales are then determined by fitting either power laws (Martin et al. 1987) or exponential functions (Armstrong et al. 2002) to the vertical profiles of POC flux. However, these methods are respectively limited by their spatial resolution, vertical resolution, and integration across different temporal and spatial domains. The methods also provide conflicting results on the spatial patterns of regeneration depths, precluding the development of a comprehensive mechanistic understanding of the processes that control POC regeneration (Henson et al. 2012; Marsay et al. 2015).

We determine POC regeneration length scales in the eastern tropical South Pacific by adapting the paleoceanographic $^{230}$Th-normalization method (Francois et al. 2004) to
the water column. Our study is the first application of this approach to generate internally consistent, high-resolution POC flux profiles that resolve differences in POC flux characteristics across biogeochemical gradients on annual to multiannual time scales. By analyzing particulate $^{230}$Th ($^{230}$Th$_p$) and POC collected by in-situ filtration, we calculate POC fluxes, integrated across ~1- to 3-y time scales, at each measurement depth (Anderson et al. 2016; Hirose 2006) (See Section 3.2). A recent intercomparison of sediment trap and radiochemical methods at the Bermuda Atlantic Time-Series Station found that $^{230}$Th$_p$-normalized POC fluxes agreed (within 2-σ uncertainty) with other radiochemical methods for estimating POC flux in the upper water column (Hayes et al. 2018a). In further support of this approach, we find that $^{230}$Th$_p$-derived POC fluxes on the GEOTRACES GP16 transect are within uncertainty of nearby annually averaged sediment trap POC fluxes (Figure S3.1). Samples were collected on the GP16 transect (Research Vessel Thomas G. Thompson, cruise TN303) spanning from Peru to Tahiti (Figure 3.1). The GP16 section traversed a strong zonal gradient in upper water column conditions, particularly in productivity and subsurface O$_2$ (Figure 3.1). The Peru oxygen-deficient zone (ODZ) in the eastern portion of the section hosts nanomolar to subnanomolar O$_2$ levels, making it functionally anoxic (Thamdrup et al. 2012). Oxygen concentration minima from GP16 were below the detection limit of 1 μmol/kg at stations 1 to 13 (Figure 3.1b). Pigment and fluorescence data indicate that there is a transition in microbial community structure moving offshore within the ODZ, from autotrophic at station 9 to heterotrophic at station 11 (Ohnemus et al. 2017). Our $^{230}$Th-normalized POC flux profiles have sufficient vertical resolution to provide statistically significant constraints on the spatial variability and mechanisms controlling POC regeneration length scales and carbon transfer to the
3.2 Materials and Methods

3.2.1 Particulate Sample Collection

Particulate samples on the GP16 section were collected via in-situ filtration using McLane pumps (WTS-LV) with two flow paths. Each flow path was equipped with a 142-mm-
diameter filter holder containing baffles to ensure homogenous particle distributions on
the filters (Bishop et al. 2012). The holders both had a 51-μm Sefar Polyester mesh prefilter,
followed by either paired acid-leached, precombusted quartz-fiber Whatman QM-A filters
with a 1-μm pore size, or acid-leached paired Pall Supor800 0.8-μm polyethersulfone filters
(Lam et al. 2018).

Blank filters were simultaneously deployed with the pumps on each cast, either on
specially adapted filter holders disconnected from pumped water flow or in polypropylene
containers zip-tied to the frame of a pump. The blank filters were in contact with ambient
seawater at pump depth for the entire cast. These dipped blanks were used for background
corrections of POC and Th isotopes. Previous publications (Lam et al. 2018; Lee et al. 2018)
have provided more detailed documentation of the collection of in-situ pumped particles
on the TN303 cruise.

3.2.2 Sample Analysis

Measurement techniques for dissolved oxygen (Peters et al. 2018), POC (Lam et al. 2018),
and Th isotopes (Pavia et al. 2018) on the GP16 section have been previously documented.
We provide here a brief overview containing the salient details of the measurements tech-
niques, but refer readers to the publications containing the original data for complete
methods.

Dissolved oxygen was determined via modified Winkler titration, according to stan-
dard procedures established in the WOCE, CLIVAR, and GO-SHIP Repeat Hydrography
programs. The detection limit for discrete oxygen samples was 1 μmol/L, with ~0.1% pre-
cision (Peters et al. 2018). The finalized oxygen dataset is archived online at the Biological and Chemical Oceanography Data Management Office (BCO-DMO) as well as the GEOTRACES Intermediate Data Product (Schlitzer et al. 2018).

POC in the 0.8- to 51-μm small-size fraction (SSF) was measured on two 12-mm-diameter punches taken from the top QM-A filter, representing ~20 L of pumped seawater. The filters were dried at sea, fumed with concentrated hydrochloric acid (HCl) to remove inorganic carbon, and then dried again before the punches were taken. SSF POC was measured using a FlashEA 1112 Carbon/Nitrogen Analyzer using a Dynamic Flash Combustion technique. Dipped blank QM-A filters (n = 47) were used for blank subtraction, and the SD of the dipped blank measurements was assigned as the uncertainty for SSF POC measurements. POC data are available online at BCO-DMO and the GEOTRACES Intermediate Data Product (Schlitzer et al. 2018).

Particulate $^{230}$Th ($^{230}$Th$_p$) was measured in two laboratories: Lamont-Doherty Earth Observatory (LDEO), and University of Minnesota (UMN). Intercalibration showed no detectable differences between the methods of the two laboratories. At LDEO, one-fourth-filter aliquots were placed in 60-mL Savillex jars, a $^{229}$Th-$^{233}$Pa spike and 25 mg of purified iron carrier were added, and the filters sat overnight in concentrated HNO$_3$ at room temperature. The filters were then completely digested in concentrated perchloric acid (HClO$_4$) to dissolve the polyethersulfone material. Particles were subsequently digested in concentrated HNO$_3$ and HF, followed by iron coprecipitation. Thorium fractions were isolated using anion exchange chromatography (Bio-Rad AG1-X8, 100 to 200 μm). Measurements of $^{230}$Th and $^{232}$Th were made on a Thermo Element XR inductively coupled plasma mass spectrometer (ICP-MS) instrument, using an Aridus desolvating nebulizer.
for sample introduction to improve sensitivity (Choi et al. 2001). Full details of the LDEO method have been published previously (Anderson et al. 2012; Pavia et al. 2018).

At UMN, one-eighth–filter aliquots were folded into 30-mL Teflon beakers, a $^{229}$Th-$^{233}$Pa spike was added, and filters were submerged in 7N HNO$_3$ and 10 drops of concentrated HF. The beakers were capped and heated under pressure for 10 h at 200ºF to leach/digest the samples. After heating, the leach solution was quantitatively transferred to a separate 30-mL Teflon beaker, and five drops of concentrated HClO$_4$ were added. The leach solution was dried down and taken up in 2N HCl, followed by iron hydroxide coprecipitation. The precipitate was dissolved, dried down, and taken up again in 7N HNO$_3$, which was then loaded onto Bio-Rad AG1-X8 100- to 200-μm mesh resin for separation of Th fractions via anion exchange chromatography. Thorium isotope measurements were made on a Thermo Neptune multicollector ICP-MS instrument (Shen et al. 2002, 2012). In both laboratories, measured $^{230}$Th and $^{232}$Th were blank corrected using average dipped blank values. Errors in measured $^{230}$Th include uncertainties from ICP-MS counting statistics, spike concentrations, and blank corrections. Particulate $^{230}$Th and $^{232}$Th data are archived at BCO-DMO and in the GEOTRACES Intermediate Data Product (Schlitzer et al. 2018). More details on the measurements techniques in this study can be found in the Supplementary Information (Section 3.4).

### 3.2.3 Application of $^{230}$Th-normalization to POC fluxes

$^{230}$Th-normalization is a widely used method in paleoceanography for correcting sediment mass accumulation rates for syndepositional redistribution (Bacon 1984; Henderson and
Most $^{230}\text{Th}$ in seawater is produced in the water column by the decay of $^{234}\text{U}$. Uranium is highly soluble in seawater, stabilized as carbonate complexes (Djogić et al. 1986; Langmuir 1978) with a residence time of hundreds of thousands of years (Dunk et al. 2002). As such, uranium is conservative in seawater, with only minor (parts per thousand) spatial variations in concentration as a function of salinity, allowing for the prediction of oceanic uranium concentrations from salinity (Chen et al. 1986a; Owens et al. 2011). These uranium–salinity relationships are used to predict the activity of the major uranium isotope, $^{238}\text{U}$, which is multiplied by the seawater $^{234}\text{U} / ^{238}\text{U}$ activity ratio of 1.1468 (Andersen et al. 2010) to estimate $^{234}\text{U}$. Thus, the production rate of $^{230}\text{Th}$ integrated to a depth horizon $z$ can be predicted anywhere in the water column:

$$P(^{230}\text{Th})_z = \int_0^z \lambda_{^{230}\text{Th}}^{234}\text{U} \, dz$$

Unlike its parent $^{234}\text{U}$, $^{230}\text{Th}$ is highly insoluble in seawater. Upon production by $^{234}\text{U}$ decay, $^{230}\text{Th}$ rapidly adsorbs to particles, with a scavenging residence time of 20 to 40 y (Hayes et al. 2013a), much shorter than both its half-life [75,584 y (Cheng et al. 2013)] and the time scale of whole-ocean mixing. The removal of $^{230}\text{Th}$ from a given location is potentially driven by two processes: scavenging removal by particles, and lateral redistribution by advective-diffusive fluxes. Where the latter can be either ignored or corrected, the concentrations of both dissolved and particulate $^{230}\text{Th}$ are expected to increase linearly with depth in a process known as reversible scavenging (Bacon and Anderson 1982). In this formulation, the integrated production of $^{230}\text{Th}$ to a depth $z$ is balanced in one dimension by its downward export on particles sinking through that depth.
The equation for calculating $^{230}$Th$_p$-normalized POC fluxes is nearly identical to that used in paleoceanography to determine vertical constituent fluxes:

$$\text{POC Flux} = \frac{P \left( ^{230}\text{Th} \right)_z \times [\text{POC}]}{\left[ ^{230}\text{Th} \right]_p}$$ (3.2)

where the integrated production rate is in $\mu$Bq m$^{-2}$ d$^{-1}$, $\left[ ^{230}\text{Th} \right]_p$ is the activity of $^{230}$Th in $\mu$Bq m$^{-3}$, and [POC] is the concentration of POC in mmol m$^{-3}$. The resulting POC fluxes we report are in units of mmol m$^{-2}$ d$^{-1}$.

We calculate POC fluxes on particles in the 0.8- to 51-μm SSF. Due to low $^{230}$Th activity on particles >51 μm, larger filter aliquots were required for analysis than could be routinely measured across the entire section. The actual size of sinking particles carrying $^{230}$Th downward to balance its water column production is unknown. However, scavenging removal of $^{230}$Th is a two-step process involving adsorption of $^{230}$Th onto small particles, which subsequently undergo repeated cycles of aggregation into larger “sinking” particles and disaggregation into smaller “suspended” particles (Bacon et al. 1985; Wang et al. 2016). Thus, provided that the aggregation-sinking process is in equilibrium on the time scales of $^{230}$-Th removal, the POC fluxes recorded by $^{230}$Th$_p$ normalization on 0.8- to 51-μm particles will be valid.

### 3.3 Results and Discussion

GP16 $^{230}$Th$_p$-normalized POC flux profiles have highest values in the subsurface near the deep chlorophyll maximum and base of the mixed layer (Figure S3.2), and decrease sub-
Figure 3.2: $^{230}$Th$_p$-normalized POC fluxes from six representative GP16 stations. The highest POC fluxes at the surface and subsurface are found at stations 1 to 9, closest to the Peru coast. Stations 17, 26, and 36, representative of the SPSG, have lower POC fluxes. Consequently with depth. Maximum POC fluxes of 5 mmol m$^{-2}$ d$^{-1}$ are found nearest to the continental shelf in the Peru upwelling region, decreasing to 2 mmol m$^{-2}$ d$^{-1}$ in the oligotrophic South Pacific gyre (Figure 3.2). The greatest flux attenuation occurs in the upper 300 m of the water column, indicative of shallow POC regeneration. At stations 1 to 9, corresponding to the Peru ODZ, POC flux decreases rapidly through the upper oxycline, stays constant through the depths of lowest oxygen, then decreases again through the lower oxycline (Figure S3.3). The lack of POC flux attenuation within the ODZ must reflect negligible regeneration of vertically sourced POC supply from above (see Section 3.4). Regeneration length scales are traditionally expressed using a power law relation.
Figure 3.3: Power-law $b$ values for GP16 POC fluxes. Values from the GP16 section (blue bars, this study) are compared with a composite estimate from the North Pacific (green dashed line) (Martin et al. 1987), a neutrally buoyant sediment trap deployment from Station ALOHA in the North Pacific subtropical gyre (gray band) (Buesseler et al. 2007), and estimates for the SPSG derived either from combining $^{234}$Th with deep-moored sediment traps (black dashed line) (Henson et al. 2012) or from particle imaging (red dashed line) (Guidi et al. 2015).

We fit power laws of form $F_z = F_{z_0} \left( \frac{z}{z_0} \right)^{-b}$ to POC fluxes in the upper 1,000 m at each station to predict the POC flux ($F_z$) at depth $z$, relative to a reference depth $z_0$, with the exponent $b$ describing the rate of flux attenuation with depth. Because the depths of the mixed layer, the deep chlorophyll maximum, and the oxycline varied between stations (Figure S3.2), we used the depth of maximum POC flux at each station as the reference depth $z_0$ rather than interpolating onto a common reference depth (e.g., the base of the euphotic zone or 100 m) across all stations. We show in the Supplementary Information (Section 3.4) that our findings are not sensitive to the choice of reference depth.

Stations 15 to 36, west of the Peru upwelling region, have average $b$ values of 1.29 ± 0.12 (Figure 3.3), much higher (i.e., shallower, faster regeneration) than previous esti-
mates for the SPSG derived from the combination of bottom-moored sediment traps and 
$^{234}\text{Th}$ ($b = 0.52$) (Guidi et al. 2015; Henson et al. 2012) and a follow-up approach that included constraints from particle imaging ($b = 0.84$) (Guidi et al. 2015). Our results are much more consistent with neutrally buoyant sediment trap deployments in the North Pacific subtropical gyre ($b = 1.33 \pm 0.15$), which had greater resolution through the upper water column depths at which the bulk of POC regeneration occurs (Buesseler et al. 2007). Transfer efficiencies derived from $b$ values fitted to bottom-moored sediment trap observations may not be an ideal benchmark for evaluating biogeochemical model representations of POC flux and regeneration in the mesopelagic, as previously suggested (Marsay et al. 2015; Weber et al. 2016). For comparing flux attenuation in oxic and suboxic regimes, data from the suboxic stations at the depths where oxygen concentrations were near zero (60 to 600 m) were grouped, as were data from the oxic stations over the same depth range. Three correlation tests were performed — Pearson’s correlation, Spearman’s rank correlation, and Kendall’s rank correlation (also known as Kendall’s tau) — and associated P values were computed for both groups of data (Press et al. 1992). POC fluxes are constant with depth within the suboxic waters of the Peru ODZ (Figure 3.4a). Correlations of POC flux with depth from 60 to 600 m show that the stations within the ODZ have no statistically significant decrease in POC flux with depth (Figure 3.4a) while stations with no suboxic waters have highly statistically significant ($P < 10^{-10}$) decreasing POC flux in the same depth range (Figure 3.4b). Stations 1 and 7 in the Peru ODZ have lower $b$ values of 0.74 ± 0.15 and 0.66 ± 0.18, respectively, compared with a range of $b$ values from 1.11 to 1.52 at oxic stations 15 to 36 (Figure 3.3).

Previous studies have also found low $b$ values for POC flux profiles from sediment trap
deployments in ODZs, attributed to greater POC preservation under low oxygen conditions (Cavan et al. 2017; Keil et al. 2016; Van Mooy et al. 2002). However, the goodness of fit for power laws at stations 1 to 7, where the POC flux at depth is greatest and the top of the ODZ is shallowest, was much lower than at the offshore stations (Figure S3.4). The residuals of the power-law fits to stations 1 to 7 are also correlated with depth (rho = −0.66, P = 0.002), indicating that a power law fails to adequately capture the functional form of POC flux profiles at ODZ stations.

Figure 3.4: Statistical analysis of POC fluxes in suboxic and oxic station (St.) groupings. (A) POC fluxes between 60 and 600 m from suboxic stations, with correlation coefficients and P values for Pearson, Spearman, and Kendall tau correlation tests for POC flux with depth. (B) POC fluxes and correlation coefficients from oxic stations. The depth range was chosen to be broadly representative of the depths of suboxic waters in order to test for the presence of statistically significant POC regeneration at suboxic stations compared with same depths in oxic waters. The POC fluxes at suboxic stations shown here mostly come from below the depths of intense POC regeneration through the upper oxycline. (C) Bootstrapped probability distributions of flux preserved as depth approaches infinity from fitting an exponential model to GP16 POC flux data at suboxic and oxic station groupings. (D) Bootstrapped probability distributions of regeneration length scale from exponential model fits to GP16 POC flux data at suboxic and oxic station groupings.
We instead fit POC flux profiles using an exponential function (Armstrong et al. 2002; Buesseler and Boyd 2009), \( F_z = F_{z0} \exp \left( \frac{z}{L} \right) + F_\infty \), including an asymptotic flux \( F_\infty \) preserved as depth approaches infinity to quantify the effect of the ODZ on POC regeneration length scale \( (L) \) and transfer to the deep ocean. Unlike the power law, the residuals of exponential fits at ODZ stations are not significantly correlated with depth (\( \rho = -0.18, \ P = 0.40 \)). We used the exponential fits to generate bootstrapped probability distribution functions for \( L \) and \( F_\infty \) for suboxic and oxic station groupings. For each group of stations, we generated 10,000 replicate datasets via resampling with replacement and then fit the exponential function via nonlinear least-squares regression to each replicate. These 10,000 estimates for each parameter are shown in Figures 3.4c and 3.4d for \( F_\infty \) and \( (L) \), respectively.

The distributions are nearly disjoint, with suboxic stations having both shallower regeneration (Figure 3.4c) and nearly 4 times more carbon flux preserved into the deep ocean (Figure 3.4d) than oxic stations. Based on the intersection of these parameters’ estimated probability distributions, we can state with 98% and 90% confidence, respectively, that \( F_\infty \) is larger and that \( L \) is smaller for the suboxic data than for the oxic data. The median \( L \) for the suboxic data is 56 m and the median \( L \) for the oxic data is 102 m. The median \( F_\infty \) for the suboxic data is 0.36 mmol m\(^{-2}\) d\(^{-1}\) and the median \( F_\infty \) for the oxic data is 0.093 mmol m\(^{-2}\) d\(^{-1}\).

This is not simply a consequence of larger export fluxes at suboxic stations. The transfer efficiency, computed as the best-fit \( F_\infty / F_{\text{max}} \), where \( F_{\text{max}} \) is the maximum POC flux at each station, is 2 to 5 times higher at suboxic stations 5, 1, and 7 than at oxic stations (Figure S3.5). Thus, the flux profiles at suboxic stations are qualitatively and significantly
different from those at oxic stations. We argue that the low $b$ values previously inferred in ODZs overlook the importance of shallow POC regeneration in the upper oxycline. In addition to its implications for ocean carbon storage, accurately representing the vertical pattern of POC flux and regeneration in ODZs is critical for determining the depth distribution and magnitude of nitrogen loss processes (anammox and denitrification) in ODZs, which are directly linked to the supply, regeneration, and stoichiometry of organic matter flux (Babbin et al. 2014).

Our results have important implications for feedbacks in the global carbon cycle under future climate change. The oligotrophic subtropical gyres are projected to expand due to increased vertical stratification (Polovina et al. 2008; Sarmiento et al. 2004b). The efficiency of POC transport to the deep ocean in the subtropics has been debated, with bottom-moored sediment trap observations suggesting efficient subtropical C storage (Henson et al. 2012), but inverse modeling (Weber et al. 2016) and neutrally buoyant sediment trap results (Buesseler et al. 2007; Marsay et al. 2015) suggesting the opposite. Shallow subtropical POC regeneration inferred from $^{230}$Th normalization in both the North Atlantic gyre (Hayes et al. 2018a) and the South Pacific (this study) are consistent with inefficient carbon storage in the oligotrophic ocean. Thus, gyre expansion from CO$_2$ warming is predicted to drive a positive feedback involving shallower carbon regeneration and less efficient carbon sequestration in the deep ocean. ODZs are expected to expand in area and shoal under climate warming (Gilly et al. 2013; Stramma et al. 2008); however, the relative importance of increased respiration and decreased ventilation is unknown (Breitburg et al. 2018; Oschlies et al. 2018). Both $L$ and $F_\infty$ are well-correlated with the depth of the upper oxycline (Ohnemus et al. 2017) (Figure 3.5), indicating that changes
in ODZ extent and POC regeneration will be intimately coupled. Our results show that regeneration dynamics in ODZ regions have two potentially very large, offsetting effects on ocean carbon storage. Shallower regeneration length scales will return respired CO$_2$ to the atmosphere more quickly, but greater POC preservation to depths below 1,000 m will result in greater abyssal carbon storage. The expansion and shoaling of ODZs, therefore, will not necessarily result in enhanced overall ocean carbon storage, as previously proposed (Cavan et al. 2017). The feedbacks between ODZ expansion and ocean carbon storage will require the implementation of more flexible and spatially variable regeneration length scales in global carbon cycle models and should be a high priority target for
future study.

3.4 Supplementary Information

Determining Unsupported $^{230}$Th$_{xs}$ for Computing POC Fluxes

Calculating $^{230}$Th-normalized fluxes requires that the $^{230}$Th is only sourced from the decay of $^{234}$U in the water column. However, there is lithogenic particulate $^{230}$Th from two separate sources: $^{230}$Th supported by $^{234}$U in the mineral lattice of detrital particles brought to the ocean by dust or resuspended sediments, and $^{230}$Th released during sediment dissolution that subsequently adsorbs onto particles (Hayes et al. 2015b). This correction is performed by subtracting the product of measured particulate $^{232}$Th and the lithogenic $^{230}$Th/$^{232}$Th ratio (4x10$^{-6}$ mole/mole) (Roy-Barman et al. 2009) from measured $^{230}$Th$_p$. All $^{230}$Th$_p$ data reported in this paper and used in flux calculations are corrected in this manner. Additional uncertainties from the measured $^{232}$Th$_p$ and a nominal 30% uncertainty in the lithogenic $^{230}$Th/$^{232}$Th ratio are propagated into the reported error in $^{230}$Th$_p$.

Total $^{230}$Th is computed as the sum of small particulate and dissolved $^{230}$Th. Where possible, dissolved samples were taken at identical depths as particulate samples, but otherwise were interpolated onto the depths of $^{230}$Th$_p$ for calculating total $^{230}$Th. Full details of the methods for collecting and measuring dissolved $^{230}$Th on the GP16 section have been previously reported (Pavia et al. 2018). Samples were taken from a conventional stainless-steel rosette in Niskin bottles, and 4-5 liters of water were filtered through a 0.45μm Acropak capsule filter. The samples were acidified to pH=2 at sea using 6M ul-
trapure HCl to prevent adsorption of Th to cubitainer walls during transport to shore (Anderson et al. 2012). In the lab, samples were weighed and spiked with $^{229}$Th-$^{233}$Pa, co-precipitated with iron oxyhydroxide, and digested in HNO$_3$, HF, and HClO$_4$. Separation of Th fractions by anion exchange chromatography and measurement by ICP-MS followed the same methodology described for particulate samples. Measured dissolved $^{230}$Th was corrected for ingrowth by $^{234}$U during sample storage.

Testing Possible Biases in $^{230}$Th-derived POC fluxes

We test the validity of using the 0.8-51μm particle size class by comparing $^{230}$Th$_{p}$-normalized 0.8-51μm POC fluxes with results from annually-averaged bottom-moored sediment traps. Hayes et al. (2018a) found that $^{230}$Th$_{p}$-derived POC fluxes below 1000m were within 8% and 21% of multi-year averages from collocated deep moored sediment traps at the Bermuda Atlantic Time-Series. On the GP16 section, $^{230}$Th$_{p}$-derived POC fluxes agree closely with annual POC fluxes from nearby deep sediment traps (Berelson et al. 2015; Hernes et al. 2001). At 135ºW, sediment trap POC fluxes are within 1-sigma uncertainty of $^{230}$Th$_{p}$-derived fluxes at similar depths (Figure S3.1a), while at 100ºW, $^{230}$Th$_{p}$-normalized fluxes at 14ºS and 16ºS are halfway between the sediment trap values at 10ºS and 20ºS, capturing the regional latitudinal productivity gradient (Figure S3.1b). The close agreement between the $^{230}$Th$_{p}$-normalized fluxes of 0.8-51 μm POC and sediment trap estimates indicates that aggregation-disaggregation between small and large particles is of primary importance for the downward transfer of POC in the mesopelagic and bathypelagic, in agreement with optical particle observations (Kiko et al. 2017) and biomarker
$^{13}$C results (Close et al. 2013).

We test whether size fractionation is a potential bias by comparing >51μm and 0.8-51μm POC/$^{230}$Th$_{p}$ ratios for the limited number of samples for which it was possible to analyze both size fractions (Figure S3.6). POC/$^{230}$Th$_{p}$ is 29±6% higher in the >51μm size fraction (n=23, $R^2$=0.95), but there is no appreciable trend in size fractionation with depth. Not including a single high POC/$^{230}$Th$_{p}$ value in both size fractions from station 7 that drives the most of the correlation, the best-fit POC/$^{230}$Th$_{p}$ slope is 1.05±0.11 (n=22, $R^2$=0.8), within uncertainty of unity (Figure S3.6). So, while it is possible that our fluxes derived from 0.8-51μm particles slightly underestimate the overall POC flux, this should not affect our interpretation of the shape of the profiles (i.e., the gradient with depth in the POC flux).

The POC fluxes we observe are also not influenced by lateral transport of organic matter from the continental shelf. Sanial et al. (2018) measured $^{228}$Ra, which is supplied by diffusion from sediments and thus traces the advection of material from the continental shelf, on the GP16 section. While $^{228}$Ra is enriched in the surface stations from the shelf to the open ocean, the enrichment is mostly confined to oxic waters above the OMZ, indicating low lateral inputs of shelf-derived material to ODZ depths (2018). Additionally, the offshore gradient in POC flux within the ODZ is minimal (Figure 3.1, Figure S3.3), whereas lateral transport of POC from the shelf would likely cause there to be much higher POC fluxes near the shelf that drop off rapidly towards the open ocean.

Application of $^{230}$Th$_{p}$-normalization requires there to be no net advective and/or diffusive gain or loss of $^{230}$Th in the water column. Lateral transport of $^{230}$Th could potentially bias $^{230}$Th-normalized fluxes. High particle fluxes in productive regions could result in
lower dissolved $^{230}$Th concentrations than in oligotrophic regions with low particle fluxes. Lateral eddy diffusion could then transport $^{230}$Th from the interior towards the margin, a process known as boundary scavenging (Bacon et al. 1976; Spencer et al. 1981). The short residence time of $^{230}$Th generally limits its redistribution by lateral isopycnal diffusion (Hayes et al. 2013a), and annually-averaged sediment trap fluxes of $^{230}$Th are typically within 10-15% of the production rate in the overlying water column (Yu et al. 2001). A slight zonal gradient in dissolved and total $^{230}$Th is apparent in our profiles below 400m (Figure S3.7). Net shoreward transport of $^{230}$Th by mixing would act to increase the apparent $^{230}$Th$_{p}$-normalized POC fluxes at sites further offshore, and decrease them close to shore. However, there is no discernable feature in the POC flux profiles below 400m that would indicate shoreward transport of $^{230}$Th at these depths, and the bulk of the differences between POC flux profiles is above the depths where there is an offshore $^{230}$Th gradient. Additionally, both surface (Black et al. 2018) and 400m subsurface (Czeschel et al. 2011) net zonal flows at 8-12°S are negligible. Thus, lateral transport by either advection or eddy diffusion does not impact our results.

Upwelling rates of 0-3 m d$^{-1}$ have been estimated in nearshore waters off Peru using $^{3}$He and $^{7}$Be methods (18-20). Since total $^{230}$Th increases with depth, upwelling can transport $^{230}$Th upward through the base of the mixed layer. In this case, the sinking flux of particulate $^{230}$Th will be balanced by its production from $^{234}$U decay and its supply from upwelling. Adding an upwelling flux would increase the $^{230}$Th$_{p}$-derived POC flux estimates in the uppermost water column, making our maximum flux estimates a lower bound. However, we focus our interpretations on the depth-dependence of POC regeneration rates, which is not influenced by upwelling. If the shape of the regeneration profile
were dictated by the upwelling of $^{230}\text{Th}$, we would expect this to be a consistent feature across stations influenced by upwelling, whereas the regeneration features instead track the depth of the oxycline (Figure 3.5). Further, performing statistical analysis of the POC regeneration length scales only by station groupings averages out any potential effects of upwelling at a single station.

**Testing Possible Biases in Choice of Reference Depth**

The choice of reference depth can affect the $b$ values for power law fits of POC flux profiles (Buesseler and Boyd 2009). We compare $b$ and reference depth $z_0$ from the GP16 section (Figure S3.8), finding a weak positive correlation between $b$ and $z_0$ ($R^2=0.27$, $p=0.034$, $n=17$). This correlation is in the opposite direction of what we would expect to find if shallow reference depths were driving artificially high $b$ values. We also show that the location of reference depth relative to the MLD and DCM does not bias our $b$ estimates.

At some stations, the reference depth $z_0$ falls slightly above the DCM (15,21,23,25,28) or above both the DCM and MLD (5,11,13,17,26). In these cases, the POC/$^{230}$Th ratio could potentially be offset from the POC/$^{230}$Th ratio of sinking particles due to the contribution of POC from newly produced, non-sinking particles that are recycled in-situ. We test whether the inclusion of these stations biases our fitting procedures. The mean of $b$ values from stations where $z_0$ is above the DCM and/or MLD (5,11,13,17,21,23,25,26,28) is $1.18\pm0.34$, within uncertainty and very close to the mean $b$ value of $1.09\pm0.26$ from stations where $z_0$ is below the MLD and DCM (1,7,9,30,32,36). Limiting the comparison only to offshore stations (11-36), the stations with $z_0$ above the DCM only (15,21,23,25,28) have
a mean $b$ value of $1.3\pm0.16$, within error of and similar to the mean $b$ values of $1.24\pm0.12$ from stations with $z_0$ above both the MLD and DCM (11,13,17,26), and of $1.23\pm0.11$ from stations where $z_0$ is deeper than both the DCM and MLD (30,32,36). We also re-fit the exponential functions at stations 11 and 13 using $z_0$ as the first sampling depth below the MLD and DCM to test whether the correlation in Fig. 5 is an artifact of the choice of reference depth. In this sensitivity test, the correlation between oxycline depth and $L$ still holds, with $R^2=0.72$, as does the correlation between oxycline depth and $F_\infty$, with $R^2=0.69$. We thus conclude that neither our $b$ values, nor the correlation between oxycline depth and regeneration characteristics from exponential fitting, are artifacts of the choice of reference depth.
Figure S3.1: Comparison between GP16 $^{230}$Th$_p$-normalized POC fluxes and sediment trap estimates. $^{230}$Th$_p$-normalized fluxes from stations zonally-bracketing the sediment trap longitudes are shown as black and gray dots. Annually-averaged sediment trap fluxes are shown as blue stars or blue triangles. a, Comparison between GP16 stations 28 and 30 with sediment trap fluxes from the JGOFS program (12ºS, 135ºW), deployed in 1992 (Hernes et al. 2001). b, Comparison between GP16 stations 13 and 15 at 14ºS and 16ºS with sediment trap deployments from 2010-2011 at 10ºS and 20ºS along 100ºW (Berelson et al. 2015).

Figure S3.2: Depth of Maximum POC Flux (this study), Mixed Layer Depth (MLD) (Ohnemus et al. 2017) and Deep Chlorophyll Maximum (DCM) (Ohnemus et al. 2017). Station 18 is omitted because there were no $^{230}$Th$_p$ measurements on samples above 150m. Stations are oriented from east (right) to west (left).
Figure S3.3: POC Fluxes (blue symbols) and Oxygen Profiles (dashed lines) at GP16 Stations 1-13. Station order is shown from east to west going right to left. The length scale of POC flux attenuation tracks the depth of the upper oxycline at these stations.

Figure S3.4: $R^2$ values for power law fits to POC flux data. Fits are poorer at stations 5, 1, and 7, where the upper oxycline is shallowest, indicating the power laws do not properly represent the functional form of POC flux profiles at ODZ stations.
Figure S3.5: Transfer efficiencies for POC fluxes. Values are computed as the ratio between the best-fit $F_\infty$ from exponential fits to POC flux profiles and the observed maximum POC flux at each station. Highest values at suboxic stations 5, 1, and 7 indicate greater POC preservation at the stations with thickest ODZs.
Figure S3.6: Size Partitioning of POC/$^{230}$Th. Dots show individual data points of POC/$^{230}$Th ratios in large size fraction particles (LSF, >51μm) and small size fraction particles (SSF, 0.8-51μm), colored by depth. Dashed line black shows the best-fit line (slope=1.29, n=23, $R^2=0.9$) for all data points. Since much of the correlation is driven by a single high POC/$^{230}$Th ratio point from 750m at Station 7, we also fit the data without this point – the best fit line excluding this point is shown as a dashed red line (slope=1.05, n=22, $R^2=0.81$). The 1:1 line is shown as a solid black line.

Figure S3.7: $^{230}$Th Profiles and POC/$^{230}$Th ratios. a, Total $^{230}$Th. b, Particulate $^{230}$Th. c, Dissolved $^{230}$Th. d, POC/$^{230}$Th$_p$ ratios. Data from ODZ stations are shown as triangles.
Figure S3.8: Relationship of $b$ values and reference depth $z_0$. Dots show points from individual stations. Dashed line shows the least-squares linear fit to the data, which are weakly correlated with slope $0.005\pm0.002$ ($R^2=0.27$, $p=0.034$, $n=17$).
Chapter 4

*Transport and Scavenging of* \(^{231}\text{Pa}\) and \(^{230}\text{Th}\) *in the Pacific Southern Ocean*

**Abstract**

The Southern Ocean hosts complex connections between ocean physics, chemistry, and biology. Changes in these connections are hypothesized to be responsible for significant alterations of ocean biogeochemistry and carbon storage both on glacial-interglacial timescales, and in the future due to anthropogenic forcing. Isotopes of thorium (\(^{230}\text{Th}\), \(^{232}\text{Th}\)) and protactinium (\(^{231}\text{Pa}\)) have been widely applied as tools to study paleoceanographic conditions in the Southern Ocean. However, understanding of the chemical behavior of these isotopes in the modern Southern Ocean has been limited by a paucity of high-resolution observations. In this study, we present measurements of dissolved \(^{230}\text{Th}\), \(^{232}\text{Th}\), and \(^{231}\text{Pa}\) on a meridional transect along 170\(^\circ\)W from 67\(^\circ\)S to 54\(^\circ\)S in the Pacific sector of the Southern Ocean, with high vertical and meridional sampling resolution. We find Th/Pa fractionation factors below 1, highlighting the preferential removal of Pa relative to Th in a region where the particle flux is dominated by biogenic opal, with low lithogenic inputs. We also find steep gradients in all three of these isotopes along neutral density surfaces from north to south, highlighting the importance of isopycnal mixing in trans-
porting these nuclides to the Southern Ocean. Our results suggest that $^{231}\text{Pa}$ and $^{230}\text{Th}$ in the Southern Ocean are highly sensitive tracers of physical transport, and may find use in studies of Southern Ocean biogeochemical-physical connections in past, present, and future.

### 4.1 Introduction

The Southern Ocean is a critical valve connecting the physical and chemical properties of the deep ocean with the surface ocean and atmosphere. In the Southern Ocean, strong westerly winds drive upwelling of nutrient- and carbon-rich deep waters towards the surface, where these waters are either carried southward to form Antarctic Bottom Water around the Antarctic continent (e.g. Marshall and Speer 2012), or northward where they degas natural $\text{CO}_2$ and take up anthropogenic $\text{CO}_2$ from the atmosphere (Gruber et al. 2009) before subducting to form intermediate waters. Because of limiting levels of iron and light, phytoplankton are unable to fully drawdown upwelled DIC and nutrients in the surface of the Southern Ocean, causing both intermediate and deep waters to subduct with significant preformed nutrient contents (Sarmiento et al. 2004a; Sigman and Boyle 2000). It is hypothesized that greater nutrient utilization due to enhanced dust inputs and increased stratification in the Southern Ocean led to significant drawdown of atmospheric $\rho\text{CO}_2$ during the last glacial period, stemming the ‘leak’ of $\text{CO}_2$ from the Southern Ocean via increased efficiency of the biological pump (Martínez-Garcia et al. 2014; Siegenthaler and Wenk 1984; Sigman and Boyle 2000). Thus, it is critical to study the interactions between physics, chemistry, and biology in the Southern Ocean to understand the global
The long-lived isotopes of thorium (\(^{230}\)Th, \(^{232}\)Th) and protactinium (\(^{231}\)Pa) can be used as tracers of particle dynamics and physical transport in both modern and paleo applications. Primordial \(^{232}\)Th is delivered to the ocean by the dissolution of lithogenic materials like continental dust. The radiogenic isotopes \(^{230}\)Th and \(^{231}\)Pa are produced in-situ by the decay of uranium (\(^{234}\)U \(\rightarrow^{230}\)Th, \(^{235}\)U \(\rightarrow^{231}\)Pa). While uranium is highly soluble and well-mixed in the oceans, varying only as a function of salinity (Owens et al. 2011), Th and Pa are highly insoluble, with typical water column scavenging residence times of 10-40 years for \(^{230}\)Th and 50-200 years for \(^{231}\)Pa (Henderson and Anderson 2003) that are much shorter than their respective half-lives of 75,584 years (Cheng et al. 2013) and 32,760 years (Robert et al. 1969). As a result, \(^{230}\)Th and \(^{231}\)Pa are removed nearly quantitatively in 1-dimension relative to their known water column production rates from U decay. In the absence of lateral redistribution, the burial ratio of \(^{231}\)Pa/\(^{230}\)Th would be equal to their water column production ratio (0.093, activity ratio).

Protactinium and thorium have differing sensitivities to many variables that can affect their water column distributions, including particle composition, particle flux, and lateral transport by advection and eddy diffusion. The Southern Ocean is a somewhat unique locale for Pa and Th dynamics. Elevated diatom productivity occurs where nutrient-rich deep waters reach the surface (Nelson et al. 2002), causing diatom opal to dominate the bulk particle flux beneath these areas (Honjo et al. 2000). Biogenic opal has an exceptionally high affinity for removing \(^{231}\)Pa compared to other particle types like lithogenics, CaCO\(_3\), and organic matter (e.g. Chase et al. 2002; Geibert and Usbeck 2004). As a result, \(^{231}\)Pa/\(^{230}\)Th ratios in Southern Ocean sediment traps (Chase et al. 2003), in-situ
pumped particulate matter (Venchiarutti et al. 2011; Walter et al. 1997) and surface sediments (Bradtmiller et al. 2009; Chase et al. 2003; DeMaster 1981; Walter et al. 1997) exceed the production ratio of 0.093, necessitating greater net transport of $^{231}$Pa into the Southern Ocean compared to $^{230}$Th. The close coupling of opal fluxes and $^{231}$Pa/$^{230}$Th ratios has also led to the use of sedimentary $^{231}$Pa/$^{230}$Th as a paleo-proxy for past changes in diatom productivity, and thus nutrient supply from upwelling, in the Southern Ocean (Anderson et al. 2009; Kumar et al. 1995).

Previous studies of dissolved and/or total (i.e. dissolved+particulate) $^{231}$Pa and $^{230}$Th in Southern Ocean waters have found negligible meridional gradients along isopycnals for these nuclides, suggesting that advection of deep waters towards the surface from north to south, rather than diffusive mixing, is responsible for $^{231}$Pa transport into the Southern Ocean (Chase et al. 2003; Roy-Barman et al. 2019; Rutgers van der Loeff and Berger 1993; Rutgers van der Loeff et al. 2016; Venchiarutti et al. 2011). However, most of these observations have come from the Atlantic sector of the Southern Ocean, and only measurements of total $^{231}$Pa and $^{230}$Th exist from the Pacific Sector, with low vertical resolution in the upper 1500m (Chase et al. 2003). Additionally, these studies typically have stations spaced ~5° of latitude apart, preventing identification of gradients on finer scales.

In this study, we measured dissolved $^{231}$Pa, $^{230}$Th, and $^{232}$Th along the NBP1702 section at 170°W in the Southern Ocean. This section reoccupied the AESOPS transect from the U.S. JGOFS program (Smith Jr. et al. 2000), where measurements of total $^{231}$Pa and $^{230}$Th were previously made (Chase et al. 2003). We first use several measurements of size-fractionated dissolved samples to study the physical speciation of $^{231}$Pa and $^{230}$Th in
near-surface waters. We also present measurements from 12 profiles with an average meridional spacing of 1° of latitude, with 10-12 measurements in the upper 1500-2000m at each location. We find high $^{232}\text{Th}$ and $^{230}\text{Th}$ concentrations in the Ross Gyre, and discuss the limitations of using paired Th isotopes in the upper water column to estimate dust fluxes in upwelling regions. Combining our data with historical sediment trap observations, we determine the relative scavenging intensity of $^{231}\text{Pa}$ and $^{230}\text{Th}$. Finally, we document the first evidence for steep north-south isopycnal gradients in dissolved $^{231}\text{Pa}$ and $^{230}\text{Th}$, and suggest that isopycnal mixing may play an important role in the transport of $^{231}\text{Pa}$ into the Southern Ocean.

4.2 Materials and Methods

4.2.1 Hydrographic Setting

Samples were taken along a meridional transect from 67°S to 54°S at 170°W, spanning the Ross Gyre poleward of the Southern Boundary of the Antarctic Circumpolar Current (SBACC); the Antarctic Zone (AZ) between the SBACC and the Antarctic Polar Front (APF); the Polar Frontal Zone (PFZ) between the APF and the Subantarctic Front (SAF), and the Subantarctic Zone north of the SAF (Figure 4.1). The modes of fluid motion, particle flux, and nutrient supply in these various regions are sufficiently diverse to merit an explanation of their hydrographic features.

The ACC is forced by strong westerly surface winds driving divergence and Ekman upwelling, drawing up waters from the deep ocean along isopycnals sloping upwards
Figure 4.1: Site map of sampling locations during NBP1702. Individual stations are shown as stars and labeled with their station number. GEBCO 6x6 minute bathymetry is shown in color. The location of climatological fronts (Orsi et al. 1995) are shown as solid lines, including the Subtropical Front (STF) in white, the Subantarctic Front (SAF) in green, the Antarctic Polar Front (APF) in black, and the Southern Boundary of the Antarctic Circumpolar Current (SBACC) in red.

from north to south, resulting in eastward geostrophic flow around the Antarctic Continent. The waters upwelling in the Southern Ocean are primarily Circumpolar Deepwater (CDW), which is further subdivided into Upper Circumpolar Deepwater (UCDW; low $O_2$, high nutrients) and Lower Circumpolar Deepwater (LCDW; higher $O_2$, higher salinity). On NBP1702, UCDW can be identified by an $O_2$ minimum between the neutral density surfaces $27.6 <= \gamma_n <= 27.95$, sitting above the higher-salinity LCDW found at $\gamma_n > 27.95$ (Figure 4.2). UCDW and LCDW upwell from below 1000m at the northern end of the NBP1702 section to <250m depth at 65ºS where the isopycnals flatten southward (Figure 4.2).

Above 250m, waters south of the APF are stratified into two layers typical of austral summer, with warmer, fresher Antarctic Surface Water (AASW) at the surface atop
Figure 4.2: Hydrographic features on the NBP1702 section. Top panel shows CTD temperature, middle panel shows CTD salinity, and bottom panel shows CTD oxygen. Individual neutral density surfaces between 27.6-28.1 kg/m$^3$ are contoured in each panel.
colder, saltier Winter Water (WW) which forms a subsurface temperature minimum at 100-200m. The Winter Water is a remnant from deep winter mixing (Toole 1981), while AASW freshens during summer from precipitation and ice melt (Chaigneau et al. 2004; Park et al. 1998). The northward persistence of this subsurface temperature minimum (<2°C) can be used to distinguish the northward extent of the APF (Orsi et al. 1995). On NBP1702, this temperature minimum is found at 59ºS (Figure 4.2), putting the APF ~2º further north than in Orsi et al. (1995). This is unlikely to be due to seasonality, as satellite reconstructions of the APF location suggest poleward front migration during austral spring and summer (Freeman et al. 2016).

Ekman upwelling, isopycnal mixing, and deep wintertime diapycnal mixing supply macro- and micro-nutrients like Si(OH)$_4$, NO$_3^-$, and Fe that fuel diatom productivity. During the winter, more intense mixing and low biological uptake allows for net accumulation of nutrients, while intense diatom blooms during spring and summer result in slight NO$_3^-$ drawdown (Morrison et al. 2001) and nearly complete Si(OH)$_4$ drawdown (Sigmon et al. 2002). These blooms result in sharp latitudinal Si(OH)$_4$ gradients in the spring and summer (Brzezinski et al. 2001). On NBP1702, surface Si(OH)$_4$ was below 3 µmol/L everywhere north of 62ºS, sharply increased to 20 µmol/L at 63ºS, then steadily increased poleward to 61 µmol/L at 67ºS (Figure 4.3). Active diatom productivity was evident from ~50m biogenic silica (bSi) peaks >10 µmol/L at 62-63ºS, with smaller peaks of ~5 µmol/L at 61ºS and 64ºS (Figure 4.3).
4.2.2 Sample Collection

Most samples were collected in Niskin bottles deployed on a conventional stainless steel rosette. Methods for the collection and measurement of Si(OH)$_4$, and bSi are detailed in Robinson et al. (in prep). Each sample (~4-5L) for Th and Pa isotope analysis was filtered through a 0.45 µm Acropak capsule filter into an acid-cleaned cubitainer and acidified to pH=2 using 6M hydrochloric acid at sea, following GEOTRACES protocols (Anderson et al. 2012). In addition, several near-surface seawater samples were collected to determine
the size fractionation of dissolved Th and Pa isotopes. These samples were collected using a PFA-coated PTFE bellows pump deployed at approximately 10m depth, with seawater passed through tubing running from the pump to a clean bubble in the ship’s lab. There, approximately 5L of water was collected for Th and Pa analysis by filtration over either a 0.2 µm or 0.02 µm capsule filter, collected in an acid-cleaned cubitainer, and acidified to pH=2 using 6M hydrochloric acid at sea.

4.2.3 Sample Analysis

Samples were analyzed on-shore using previously published methods for analysis of sea-water Th and Pa isotopes at LDEO (Anderson et al. 2012; Pavia et al. 2019b; Pavia et al. 2018). Samples were spiked with $^{229}$Th and $^{233}$Pa and 15mg of dissolved Fe was added as Fe(NO$_3$)$_3$, and allowed to equilibrate for 24 hours. The samples were then raised to pH=8.3-8.7 by adding ~8-10 mL of concentrated Optima grade NH$_4$OH to precipitate Fe as Fe oxyhydroxide, and allowed to settle for 2 days. The overlying water was drained, and the Fe precipitate was centrifuged and washed in Milli-Q water before digestion at 200°C in concentrated HNO$_3$, HF, and HClO$_4$. After dissolution, the samples were dried down and brought back up in concentrated HCl for separation of Th and Pa fractions via anion exchange chromatography on Bio-rad AG1-X8 100-200 mesh size resin. 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 in peak jumping mode.

Procedural blanks were determined by processing 2L of Milli-Q water in acid-cleaned
cubitainers in the same manner as seawater. Blanks were taken to sea and acidified to pH=2 at the same time as seawater samples, and analyzed on-shore using identical methods, with 2 blanks measured for every ~15 samples. Mean and 1σ procedural blanks for dissolved samples were $^{232}\text{Th}=3.7\pm 1.4$ pg, $^{230}\text{Th}=0.21\pm 0.06$ fg, and $^{231}\text{Pa}=0.03\pm 0.02$ fg. Reproducibility was assessed by measuring aliquots of two intercalibrated working standard solutions of $^{232}\text{Th}$, $^{230}\text{Th}$, and $^{231}\text{Pa}$: SW STD 2010-1 (Anderson et al. 2012), and SW STD 2015-1, which has lower $^{232}\text{Th}$ concentrations more similar to Pacific seawater conditions. For standards run alongside NBP1702 samples, the reproducibility for each isotope was 2.12% for $^{230}\text{Th}$, 0.87% for $^{232}\text{Th}$ and 1.76% for $^{231}\text{Pa}$ on SW STD 2010-1, and was 0.87% for $^{230}\text{Th}$, 3.78% for $^{232}\text{Th}$ and 2.69% for $^{231}\text{Pa}$ on SW STD 2015-1.

Dissolved $^{230}\text{Th}$ and $^{231}\text{Pa}$ were corrected for ingrowth of $^{230}\text{Th}$ and $^{231}\text{Pa}$ during sample storage using the uranium-salinity relationship of Owens et al. (2011), a seawater $^{234}\text{U}/^{238}\text{U}$ activity ratio of 1.1468 (Andersen et al. 2010), and a seawater $^{238}\text{U}/^{235}\text{U}$ molar ratio of 137.824 (Weyer et al. 2008). Dissolved $^{230}\text{Th}$ and $^{231}\text{Pa}$ were also corrected for lithogenic contributions using measured dissolved $^{232}\text{Th}$, and assuming a detrital $^{230}\text{Th}/^{232}\text{Th}$ molar ratio of 4.0x10^-6 (Roy-Barman et al. 2009), and a $^{231}\text{Pa}/^{232}\text{Th}$ molar ratio of 8.8x10^-8, derived from assuming an average upper continental crust U/Th ratio (Taylor and McLennan 1995) and secular equilibrium between $^{231}\text{Pa}$ and $^{235}\text{U}$. Typically $^{230}\text{Th}$ and $^{231}\text{Pa}$ data corrected in this manner are denoted by the subscript “xs”, but since all data shown in this paper has been corrected the same way, we will omit the subscript for clarity.
Figure 4.4: Depth profiles of dissolved $^{230}$Th (first panel), $^{231}$Pa (second panel), $^{232}$Th (third panel), and $^{231}$Pa/$^{230}$Th ratio (fourth panel) from NBP1702.
4.3 Results

On NBP1702, concave profiles are found for dissolved $^{230}$Th, $^{232}$Th, and $^{231}$Pa south of 61°S at stations 1-7, reflecting physical transport of these isotopes along upwelling isopycnal surfaces (Figure 4.4). Concentrations of $^{230}$Th, $^{232}$Th, and $^{231}$Pa below 100m increase from north to south, with the largest lateral gradients at depth for $^{230}$Th and $^{231}$Pa found between ~64°S (Stn. 4) and ~63°S (Stn 5). Dissolved $^{231}$Pa/$^{230}$Th activity ratios decrease from the surface to ~150m depth, below which the ratios stay constant to 1000-1500m, with values increasing northward from 0.35 at 67°S to 0.6 at 54°S (Figure 4.4).

For much of the section north of 61°S, isopleths of $^{230}$Th and $^{231}$Pa follow upwelling neutral density surfaces as they upwell (Figure 4.5). However, near the APF this quasi-conservative behavior breaks down, with steep gradients opening up for $^{231}$Pa (~61°S) further to the north than for $^{230}$Th (~64°S) (Figure 4.5). The 61-64°S region of most pronounced $^{231}$Pa removal directly coincides with the highest levels of biogenic silica measured on the section (Figure 4.3).

4.4 Discussion

4.4.1 Physical Speciation of Dissolved Th and Pa

Ions in seawater are assigned to be in the dissolved phase based on an operational definition (e.g. passing through a 0.2-µm or 0.45-µm filter). However, colloids (e.g. Wells and Goldberg 1992), including metal-binding organic ligands (van den Berg 1995), pass through these filters and generate additional size fractionation within the operationally-
Figure 4.5: Section plots of dissolved $^{230}$Th (top panel) and $^{231}$Pa (bottom panel) from NBP1702 with neutral density contours.

Defined dissolved phase between "soluble" (typically <kDa or <0.02-$\mu$m) and "colloidal" (between 10kDa or 0.02-$\mu$m and 0.2-$\mu$m or 0.45-$\mu$m). Significant fractions of dissolved metals including iron (Fitzsimmons et al. 2015a,b) and copper (Roshan and Wu 2018) are found in the colloidal phase, while some reactive metals such as dissolved Al and Ti have nearly no colloidal component (Dammshäuser and Croot 2012).

Understanding the size speciation of Th and Pa isotopes is important for multiple reasons. Adsorption to colloids and subsequent aggregation has been hypothesized to be
an important mechanism for the scavenging removal of Th (Honeyman and Santschi 1989; Honeyman et al. 1988a). Thus, determining the partitioning of Th and Pa into colloidal phases could serve as a test of this hypothesis. Additionally, applications of Th isotopes to quantify oceanic fluxes such as aerosol dust deposition (Hayes et al. 2013b; Hirose and Sugimura 1987; Hsieh et al. 2011) and lithogenic boundary inputs (Hayes et al. 2013b) require the assumption of identical scavenging rates for $^{230}$Th and $^{232}$Th. With unique sources of in-situ production by $^{234}$U decay ($^{230}$Th) and dissolution of lithogenic matter ($^{232}$Th), differential incorporation into colloids could potentially decouple the reactivity of the two isotopes.

Studies using cross-flow filtration have not found such a phenomenon, though existing data are extremely limited (<10 total measurements). In the oligotrophic North Pacific (Hayes et al. 2015c), the high-dust eastern North Atlantic (Hayes et al. 2017), low fractions of colloidal Th were found (<20% of total dissolved), and no significant size fractionation between $^{230}$Th and $^{232}$Th was observed (see also Roy-Barman et al. 2002). While there are no colloidal measurements from the section, anomalously high dissolved $^{232}$Th/$^{230}$Th ratios were observed in a hydrothermal plume on the GEOTRACES GP16 sections, the cause of which was argued to be a hydrothermal source of unreactive $^{232}$Th-bearing colloids (Pavia et al. 2018), which represents the primary evidence for decoupled scavenging behavior of $^{232}$Th and $^{230}$Th. To date, there have been no measurements of dissolved $^{231}$Pa size speciation.

Our results for $^{230}$Th and $^{232}$Th are difficult to interpret. Samples collected via the PFA pump were passed through either a 0.2-µm or 0.02-µm filter. The $^{230}$Th and $^{232}$Th concentrations are statistically indistinguishable between samples passed through 0.02-µm
and 0.2-µm filters at stations where samples were collected in both size fractions (Figure 4.6). Surface samples collected in Niskin bottles and subsequently filtered through 0.45-µm capsule filters were consistently offset higher than samples from the same station collected by the PFA pump and filtered at 0.2-µm or 0.02-µm, with an offset magnitude averaging 0.4±0.08 µBq/kg (1σ, n=6) for $^{230}$Th and 0.006±0.003 pmol/kg (1σ, n=5) for $^{232}$Th.

During GEOTRACES intercalibration, a small difference in Th concentrations in a 2000m sample from BATS filtered at 0.2-µm and 0.45 µm was observed, though the authors could not conclusively rule out that the difference was due to Th adsorption to the 0.2-µm Osmonics filter cartridge (Anderson et al. 2012). We similarly have difficulty ruling out methodological artifacts as driving the apparently high Th concentrations we observed in the 0.2-0.45-µm size class. The concentration of Th in this size class stays mostly constant despite large decreases in surface Th concentrations between station 1...
Figure 4.7: Percent colloidal in the size range 0.2 – 0.45 µm calculated for $^{230}$Th (blue dots), $^{231}$Pa (red diamonds), and $^{232}$Th (black squares) on surface samples collected on NBP1702. The $^{232}$Th samples at station 11 is open, as there was suspected to be $^{232}$Th contamination.

and stations 9-13 (Figure 4.6). This would imply significant increases in the percentage of dissolved Th found as colloids from south to north along the section (Figure 4.7).

Oceanographic interpretation of these results would argue for a significant proportion (up to 60%) of dissolved Th being present as colloids between 0.2-0.45µm in size, with the rest soluble (<0.02-µm). This is difficult to reconcile with results from ultrafiltration experiments, where only 10-20% of Th was found to be between 10kDa and 0.45-µm in the North Pacific (Hayes et al. 2015c), and <10% of Th was found in the same size class in the subtropical North Atlantic (Hayes et al. 2017). An alternative explanation for our results is that samples collected by the PFA pump lost Th via adsorption to the sampling apparatus,
including the pumping system and the tubing at a constant rate during sampling.

Unlike Th, there is negligible Pa found in any colloidal size class in the NBP1702 samples. At four of the six stations, %colloidal Pa is statistically indistinguishable from 0 (Figure 4.7). These results also imply that if a sampling artifact due to adsorption to PFA pump apparatus is responsible for the colloidal Th results, that adsorption to the apparatus does not seem to be an issue for Pa, consistent with previous results finding 15-20 times greater adsorption of Th than Pa to plastic bucket walls during sampling (Anderson et al. 1983a). To the best of our knowledge, these are the first measurements of physical speciation for dissolved $^{231}$Pa in the ocean, and imply the vast majority of dissolved $^{231}$Pa, at least in the Southern Ocean, is not colloidal.

We attempted to test for adsorption of Th to the plastic PFA pump tubing by analyzing a 0.1M HCl leachate of tubing used in a subsequent PFA pump deployment. We found vanishingly low concentrations of Th and Pa in the tube leachate, implying that there was insignificant adsorption to plastic tubing during sampling. Future experiments should test whether the apparent colloidal Th signal we observe is real or a methodological artifact by collecting samples using the PFA pump across 0.02-µm, 0.2-µm, and 0.45-µm filters, or by directly measuring co-located samples collected from Niskin bottles and the PFA pump that are both filtered at 0.45-µm.
4.4.2 Surface Concentrations, Th Isotope Profiles, and Implications for Dust Flux Reconstructions

The Southern Ocean stands out as a particularly important region for quantifying dust inputs, given the widespread iron limitation of primary productivity at the sea surface (Martin et al. 1990; Moore et al. 2013). Increases in dust deposition to the Subantarctic Southern Ocean during the Last Glacial Maximum stimulated increased nutrient drawdown and export production, driving drawdown of up to 40ppm of atmospheric CO2 drawdown (e.g. Martínez-Garcia et al. 2011, 2014). Quantifying the role of discrete processes (e.g. deep winter mixing, dust deposition) in delivering iron to the surface ocean requires knowledge of their supply rates, which are typically derived from global models (Tagliabue et al. 2014). However, there are a paucity of measurements of modern dust deposition rates in the Southern Ocean (Albani et al. 2014), and sedimentary methods for estimating Holocene dust deposition in the Southern Ocean are complicated by the input of ice-rafted debris (Kienast et al. 2016).

Combined measurements of dissolved $^{230}$Th and $^{232}$Th can be used to estimate dust inputs to the surface ocean (e.g. Hayes et al. 2013b; Hsieh et al. 2011). This method relies on assumptions regarding the one-dimensional mass budgets of both $^{230}$Th and $^{232}$Th. First, it requires that the scavenging removal of $^{230}$Th through a given depth horizon balances its vertically integrated production rate by $^{234}$U decay. Second, it requires that the scavenging removal of $^{232}$Th balances its input from the dissolution of continental dust.

A consistent issue with the dissolved Th isotope method for determining dust fluxes is the choice of proper integration depth. Apparent dust fluxes derived from $^{230}$Th-$^{232}$Th
typically increase in the upper 200-300m, hypothesized to be due to rapid Th export from the euphotic zone (Hayes et al. 2015c, 2017). Thus, inventories of $^{230}$Th and $^{232}$Th must be integrated beyond the depth of the euphotic zone (typically to ~250m) to capture the “true” flux of dust to the water column. The assumptions regarding the 1-d mass budgets of $^{230}$Th and $^{232}$Th must hold throughout the ~250m integration depths necessary to compute dust fluxes.

On the NPB1702 section, the mass budgets of $^{230}$Th and $^{232}$Th are likely too complex to adequately reconstruct dust inputs to the surface ocean. Concentrations of $^{230}$Th and $^{232}$Th both increase rapidly in the upper 250m, particularly at stations furthest to the south (Figure 4.4). This likely reflects the transport of these nuclides by upwelling deep waters with higher concentrations of both Th isotopes. North to south gradients in $^{230}$Th and $^{232}$Th along neutral density surfaces lighter than $\gamma_n > 27.9$ kg/m$^3$ also allow for the southward transport of these nuclides by isopycnal mixing (Figure 4.8, see Section 4.4.4). These physical supply terms to the upper 250m act as additional, difficult to quantify source of both $^{230}$Th and $^{232}$Th that invalidate the basic assumptions behind the application of Th isotopes to quantify dust flux. Studies using Th isotopes to determine dust deposition rates in regions of intense upwelling and steep isopycnal Th gradients must consider how physical transport modifies the mass budgets of both Th isotopes.

### 4.4.3 $^{230}$Th and $^{231}$Pa Distributions and Scavenging Characteristics

Profiles of dissolved $^{230}$Th and $^{231}$Pa typically increase linearly with depth in the upper 2000m due to reversible scavenging, reflecting their uniform source in seawater from U de-
cay and equilibrium adsorption/desorption on slow-sinking particles (Bacon and Anderson 1982). In the Southern Ocean, where isopycnal surfaces steeply tilt upward from north to south towards the APF, dissolved profiles of $^{230}$Th and $^{231}$Pa are concave downwards, reflecting upwelling of $^{230}$Th- and $^{231}$Pa-rich deep waters towards the surface (Chase et al. 2003; Roy-Barman et al. 2019; Rutgers van der Loeff and Berger 1993; Rutgers van der Loeff et al. 2016; Venchiarutti et al. 2011). Existing sections of $^{230}$Th and $^{231}$Pa are much more sparse, both in terms of meridional station density (typically every $\sim 5^\circ$ of latitude) and sampling depths, and all but Chase et al. (2003) are from the Atlantic sector of the Southern Ocean. Chase et al. (2003) measured total (unfiltered) Th and Pa isotopes from along the same section at 170ºW in 1998, the results of which can be qualitatively compared to our results for dissolved samples filtered at 0.45-µm.

The composition of suspended and sinking particles has been long-established as a key variable regulating the relative removal rates of $^{231}$Pa and $^{230}$Th. Diatom opal has a particularly high affinity for scavenging $^{231}$Pa, and diatom blooms near the APF drive high $^{231}$Pa/$^{230}$Th ratios both in surface sediments (Bradt miller et al. 2009; Chase et al. 2003; DeMaster 1981) and sediment trap particulate material (Chase et al. 2002) in the Southern Ocean. Sedimentary and particulate $^{231}$Pa/$^{230}$Th activity ratios above the production ratio of 0.093 in the Southern Ocean are best explained by opal particles having nearly identical affinity for removing Th and Pa from solution (Rutgers van der Loeff and Berger 1993). This affinity can be quantified via the fractionation factor $F(\text{Th/Pa})$:

\[
F \left( \frac{\text{Th}}{\text{Pa}} \right) = \frac{K_{\text{Th}}}{K_{\text{Pa}}} = \frac{[\text{Th}_p] / [\text{Th}_d]}{[\text{Pa}_p] / [\text{Pa}_d]} \tag{4.1}
\]
In regions of the ocean where the particle flux is dominated by phases other than opal like CaCO$_3$, lithogenics, and/or POC, fractionation factors are typically >10, reflecting greater particle reactivity and shorter scavenging residence time of Th compared to Pa (Hayes et al. 2015b; Moran et al. 2002). Areas rich in metalliferous particles have lower fractionation factors, reaching F<5 in the intense Southeast Pacific hydrothermal plume at 15ºS (Pavia et al. 2018). The lowest oceanic F(Th/Pa) values have been found in the Southern Ocean where the particle flux is dominated by opal, indicating that opal is the particle phase with the highest relative affinity for Pa relative to Th. In the Atlantic sector of the Southern Ocean, F(Th/Pa) is ~2 at the sea surface (Rutgers van der Loeff and Berger 1993; Venchiarutti et al. 2011), and increases linearly with depth to ~7 at 1000m (Venchiarutti et al. 2011). In the Pacific Sector on the same 170ºW line as the current study, Chase et al. (2002, 2003) combined annually-averaged sediment trap $^{231}$Pa/$^{230}$Th ratios and total (unfiltered) $^{231}$Pa/$^{230}$Th ratios to compute F(Th/Pa)<1 in the upper 1000m at 63ºS and 66ºS. However, unfiltered samples contain dissolved+particulate Th and Pa, and thus are potentially subject to biases when calculating fractionation factors.

We can recalculate the F(Th/Pa) values at 170ºW using our filtered samples for dissolved $^{230}$Th and $^{231}$Pa in combination with the historical sediment trap data. The only location where we sampled at the exact location of historical sediment trap data is at 63ºS (NBP1702 station 5, NBP9802 mooring 4). There are two ways this calculation could be performed – the first uses the dissolved $^{231}$Pa/$^{230}$Th ratio at the depth of the sediment trap (1000m), which assumes that the particles in the sediment trap have equilibrated with the waters at the same depth. The second uses the dissolved $^{231}$Pa/$^{230}$Th ratio integrated over the upper 1000m, which assumes that the particles in the sediment trap reflect scavenging
over the entire water column above the trap depth. Both methods give identical values at 1000m at 63ºS, \( F(\text{Th/Pa}) = 0.76 \), slightly lower than the original estimate of \( F(\text{Th/Pa}) = 0.88 \) from the unfiltered data of Chase et al. (2003), and consistent with preferential removal of Pa relative to Th near the APF at 170ºW.

Our results confirm zonal variability in the \( F(\text{Th/Pa}) \) between the Pacific and Atlantic sectors of the Southern Ocean. This variability is likely not due to greater diatom productivity in the Pacific sector. Annually-averaged satellite net primary productivity at the APF (Moore and Abbott 2002) near 170ºW is not substantially higher than at 0ºW (Walter et al. 1997), 50ºW (Venchiarutti et al. 2011), or 10-20ºE (Rutgers van der Loeff and Berger 1993). Instead, we propose that higher \( F(\text{Th/Pa}) \) in the South Atlantic is due to greater lithogenic dust fluxes compared to the South Pacific. The Atlantic sector of the Southern Ocean is downwind of the Patagonian dust plume, and is modeled to have \( \sim 3-5 \) times higher dust deposition than at 170ºW (Mahowald et al. 2005). Lithogenic particles have significantly higher affinity for scavenging Th than Pa, with an endmember \( F(\text{Th/Pa}) = 10 \) (Hayes et al. 2015b). Higher dust fluxes in the Atlantic SO would cause an increased proportion of the particle flux to be made up of lithogenics than in the Pacific SO, driving higher \( F(\text{Th/Pa}) \) values. As discussed in section 4.4.4, the slightly lower preference for Pa relative to Th during scavenging in the Atlantic than the Pacific may be responsible for the differing meridional gradients observed on a neutral density surface, and could potentially drive differences in the physical processes responsible for transporting Pa towards the Southern Ocean between the Atlantic and Pacific.
Figure 4.8: Dissolved Th and Pa isotopes plotted against neutral density, illustrating isopycnal gradients on the NBP1702 section. Panels from left to right show $^{230}$Th, $^{231}$Pa, $^{232}$Th, and the $^{231}$Pa/$^{230}$Th ratio.

### 4.4.4 Removal and Transport of Th and Pa Along Upwelling

**Isopycnals**

Observations of $^{230}$Th and $^{231}$Pa in the Southern Ocean have been used to construct box models of the transport and burial rates of these nuclides across different fronts and re-
regions of the ACC (Chase et al. 2003; Rutgers van der Loeff et al. 2016). These models are important for the application of sedimentary $^{231}$Pa/$^{230}$Th ratios as paleoceanographic proxies for opal flux and upwelling in the Southern Ocean (e.g. Anderson et al. 2009; Bradtmiller et al. 2009) and/or deepwater flow into the South Atlantic (Negre et al. 2010). The transport modes of $^{230}$Th and $^{231}$Pa into the Southern Ocean are also important for understanding the processes that close the budgets of these nuclides in both the Pacific (Hayes et al. 2014) and Atlantic (Deng et al. 2018; Yu et al. 1996). Box models to date typically only consider advection for the meridional transport of $^{230}$Th and $^{231}$Pa into the Southern Ocean (Luo et al. 2010). This is because dissolved $^{230}$Th and $^{231}$Pa data from the Southern Ocean have not shown significant gradients along upwelling isopycnals that would facilitate transport by eddy diffusion (Chase et al. 2003; Roy-Barman et al. 2019; Venchiarutti et al. 2011).

On NBP1702, we observe north-south isopycnal gradients for $^{230}$Th, $^{231}$Pa, and $^{232}$Th (Figure 4.8). North-south gradients along upwelling isopycnals are particularly pronounced for $^{231}$Pa, which decreases from north to south at each neutral density level sampled from station 15 at 54°S to station 3 at 65°S (Figure 4.8), with steepest gradients found between density levels $27.5 < \gamma_n < 27.7 \text{ kg/m}^3$, and $^{231}$Pa values converging between stations towards $\gamma_n \sim 28.1 \text{ kg/m}^3$. Gradients in $^{230}$Th and $^{232}$Th show similar structure to each other, though the gradients are larger for $^{232}$Th than for $^{230}$Th, with maximum north-south differences found at $\gamma_n \sim 27.7 \text{ kg/m}^3$. Unlike $^{231}$Pa, the north-south gradients in $^{230}$Th and $^{232}$Th converge at $\gamma_n \sim 27.9 \text{ kg/m}^3$, and reverse at deeper density levels, with concentrations of both Th isotopes increasing from south to north at $\gamma_n > 27.9 \text{ kg/m}^3$ (Figure 4.8).

The one-dimensional mass balance for dissolved $^{230}$Th or $^{231}$Pa, in steady-state, along
an isopycnal surface \( x \), can be written:

\[
\frac{dA}{dt} = 0 = P - J - u \frac{dA}{dx} + K_h \frac{d^2A}{dx^2} + K_z \frac{d^2A}{dz^2}
\]  

(4.2)

\( P \) is the production rate from the decay of \(^{234}\text{U} \) or \(^{235}\text{U} \), \( J \) is the removal rate by particle scavenging, and the third, fourth, and fifth terms represent dispersive fluxes due to lateral advection, isopycnal eddy diffusion, and diapycnal eddy diffusion, respectively, where \( u \) is the horizontal velocity, \( K_h \) is the isopycnal diffusivity, and \( K_z \) is the diapycnal diffusivity. Previous studies have used this equation to calculate lateral fluxes of \(^{230}\text{Th} \) from eddy diffusion in boundary scavenging regions in the North Atlantic (Hayes et al. 2015a) and to determine advective fluxes of \(^{230}\text{Th} \) from the Peru Basin to the Panama Basin in the Equatorial Pacific (Singh et al. 2013). Like these studies, we will for now ignore vertical diffusive fluxes, since we are primarily interested in the consequences of lateral redistribution for the burial locations of \(^{230}\text{Th} \) and \(^{231}\text{Pa} \).

We attempt to determine the relative impacts of diffusion and advection for \(^{230}\text{Th} \) and \(^{231}\text{Pa} \). We start by estimating the role of isopycnal diffusion, following the approach of (Hayes et al. 2015a), however we also outline a few ways this approach may be too simplistic and could be improved upon. Calculating the second derivative \( \frac{d^2A}{dx^2} \) is done on discrete density levels, and requires determining the length scales over which eddy diffusion acts on the tracers, with diffusion parameterized as a random-walk process: \( \Delta x = \sqrt{2K_h \tau} \), where \( \tau \) is the water column residence time of \(^{230}\text{Th} \) or \(^{231}\text{Pa} \). Hayes et al. (2015a) determine the residence time by dividing the water column inventories at their stations by the integrated water column production rate. However, in boundary scavenging regions
where there is net lateral influx (outflux) of a nuclide, this approach to determining residence times will overestimate (underestimate) the true residence time. Additionally, while the integrated residence time of $^{231}$Pa and $^{230}$Th increase with depth, a single length scale was used for determining lateral gradients. The length scale on which eddy diffusion acts to transport $^{230}$Th and $^{231}$Pa should thus evolve (increase) with depth as a function of the residence time. A final caveat that becomes important in the Southern Ocean is that eddy diffusivities vary both as a function of depth and latitude (e.g. Abernathey et al. 2010; Chapman and Sallée 2017). This makes the selection of a single eddy diffusivity to compute lateral fluxes extremely complex, and depending on the significance of the isopycnal gradients in eddy diffusivity, could require modifying the lateral dispersive term in the mass balance to include the eddy diffusivity in the spatial derivative.

A few of these issues can be circumvented in the Southern Ocean, though not all. For instance, the depth-integrated residence time of $^{230}$Th and $^{231}$Pa on NBP1702 cannot be determined a priori given the influence of lateral transport apparent in their concave profiles (Figure 4.8) and uncertainties in the local eddy diffusivities. However, since $F(\text{Th/Pa})$ is close to 1 averaged over the upper 1000m at 63°S (Section 4.4.3), we assert that the scavenging residence times and thus the diffusive length scales of $^{230}$Th and $^{231}$Pa are similar in this region. We use an estimate of $K_h=1000 \text{ m}^2/\text{s}$ at 170°W on the $\gamma_n=27.9 \text{ kg/m}^3$ isopycnal (Chapman and Sallée 2017) as representative for each of the isopycnals chosen, while acknowledging that this is a simplification with $\sim 50\%$ uncertainty. For now, we also assume constant residence times on each isopycnal of $\sim 15$ years for both isotopes, giving a resulting diffusive length scale $\Delta x \sim 1000 \text{ km}$. On NBP1702, 1000km is the latitudinal distance between stations 3 and 13 and we choose station 8 as the intermediate station.
Table 4.1: Second isopycnal derivatives on three neutral density surfaces for $^{230}$Th and $^{231}$Pa (in units of $\mu$bq/kg/km$^2$), as well as the activity ratio of the second derivatives for $^{231}$Pa/$^{230}$Th.

<table>
<thead>
<tr>
<th>$\gamma_n$ (kg/m$^3$)</th>
<th>$^{230}$Th $\frac{d^2\Delta}{dx^2}$</th>
<th>$^{231}$Pa $\frac{d^2\Delta}{dx^2}$</th>
<th>$\frac{^{231}\text{Pa}}{^{230}\text{Th}}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>27.5</td>
<td>1.16</td>
<td>-0.12</td>
<td>-0.11</td>
</tr>
<tr>
<td>27.7</td>
<td>7.33</td>
<td>4.71</td>
<td>0.64</td>
</tr>
<tr>
<td>28.0</td>
<td>2.44</td>
<td>5.34</td>
<td>2.18</td>
</tr>
</tbody>
</table>

The second isopycnal derivatives we calculate can be found in Table 4.1. We only performed the calculation at three discrete density levels ($\gamma_n=$27.5, 27.7, and 28.0 kg/m$^3$). The second isopycnal gradients we observe for $^{230}$Th are positive (e.g. southward flux) at each neutral density level, and have a maximum value of 7.3e-6 $\mu$bq/kg/km$^2$ at $\gamma_n=$27.7 kg/m$^3$. This is comparable to discrete values observed at 27.95<$\gamma_n<$28.05 kg/m$^3$ by Hayes et al. (2015a). Second derivatives for $^{231}$Pa were negative on the $\gamma_n=$27.5 kg/m$^3$ isopycnal (e.g. northward transport), but were positive at $\gamma_n=$27.7 kg/m$^3$, and reached a maximum at $\gamma_n=$28.0 kg/m$^3$ (Table 4.1). We can also take the ratio of the second isopycnal derivatives of $^{231}$Pa and $^{230}$Th calculated at each density level to determine the $^{231}$Pa/$^{230}$Th activity ratio transported to the Southern Ocean by mixing. The very high positive values observed at $\gamma_n=$27.7 kg/m$^3$ and $\gamma_n=$28.0 kg/m$^3$ indicate a preferential southward transport of $^{231}$Pa compared to $^{230}$Th at these density levels by isopycnal diffusion, suggesting that mixing may play an important role in driving the high sedimentary $^{231}$Pa/$^{230}$Th ratios observed in the Pacific sector of the Southern Ocean.
4.5 Summary and Outlook

Our high-resolution measurements from 170ºW offer new insights into the dynamics of scavenging and physical transport of $^{231}$Pa and $^{230}$Th in the Southern Ocean. There is intriguing evidence for unique physical speciation of $^{230}$Th in large colloids, but methodological artifacts cannot be ruled out as a cause of the finding. More work will be required to determine whether adsorption onto tubing caused samples collected by the PFA pump to have lower Th concentrations, and whether this is an issue for other reactive trace metals. We found fractionation factors F(Th/Pa) less than 1 in the upper 1000m south of the APF, indicating that $^{231}$Pa is more efficiently scavenged than $^{230}$Th. In combination with the lack of colloidal Pa, this is strong evidence for direct adsorption of Pa to opal surfaces as being the dominant driver of scavenging in the Pacific Southern Ocean. Lower F(Th/Pa) values in the Pacific sector than Atlantic sector are consistent with higher core top $^{231}$Pa/$^{230}$Th ratios in the Pacific. This difference may be due to greater dust deposition in the Atlantic sector, with the higher dust/opal ratio of particulate material in the Atlantic sector driving higher fractionation factors. Gradients in $^{231}$Pa and $^{230}$Th along neutral density surfaces from north to south suggest a strong role for isopycnal mixing in transporting these nuclides to the Southern Ocean, particularly for $^{231}$Pa. Future work incorporating $^{230}$Th and $^{231}$Pa into global models would allow for quantification of the net transport of $^{230}$Th and $^{231}$Pa to the Southern Ocean due to both advective upwelling and isopycnal diffusion.

Taken together, our results present exciting new opportunities for applying measurements of $^{231}$Pa and $^{230}$Th to study Southern Ocean physics and biogeochemistry. The im-
portance of mixing in transporting $^{231}$Pa towards the Southern Ocean should be taken into account both in mass balances of $^{231}$Pa in ocean basins (Deng et al. 2018; Hayes et al. 2014) and in paleooceanographic studies of $^{231}$Pa burial in the Southern Ocean (Anderson et al. 2009). More complex models of these nuclides could be developed by combining our measurements with velocities from the Southern Ocean State Estimate (Mazloff et al. 2010) to constrain isopycnal diffusivities and removal rates. Given their utility, $^{231}$Pa and $^{230}$Th should continue to play a key role in guiding our evolving understanding of Southern Ocean dynamics in the past, present, and future.

**Acknowledgements**

This work was supported by U.S. National Science Foundation grant OPP-1542962 to LDEO and an NSF Graduate Research Fellowship to F.J.P. (DGE-1644869). We thank the captain and crew of the R/V Nathaniel B. Palmer for their support in difficult conditions on the NBP1702 cruise.
Chapter 5

Atmospheric Dust Inputs, Iron Cycling, and Biogeochemical Connections in the South Pacific Ocean from Thorium Isotopes

Abstract

One of the primary sources of micronutrients to the sea surface in remote ocean regions is the deposition of atmospheric dust. Geographic patterns in biogeochemical processes such as primary production and nitrogen fixation that require micronutrients like iron (Fe) are modulated in part by the spatial distribution of dust supply. Global models of dust deposition rates are poorly calibrated in the open ocean, owing to the difficulty of determining dust fluxes in sparsely-sampled regions. In this study, we present new estimates of dust and iron input rates from measurements of dissolved and particulate thorium isotopes $^{230}\text{Th}$ and $^{232}\text{Th}$ on the SO245 section (GEOTRACES process study GPpr09) in the South Pacific. We first discuss high-resolution upper water column profiles of Th isotopes and the implications for the systematics of dust flux reconstructions from seawater Th measurements. We find dust fluxes in the center of the highly-oligotrophic South Pacific Gyre that are the lowest of any mean annual dust input rates measured in the global oceans, but that are consistently an order of magnitude higher than those estimated by global climate models. We also determine dust-borne Fe fluxes and re-assess the impor-
tance of individual Fe sources to the euphotic zone in the South Pacific Gyre, finding that dust dissolution, not vertical or lateral eddy diffusion, is the primary Fe source. Finally, we combine our estimates of Fe flux in dust with previously-published cellular and enzymatic quotas to determine theoretical upper limits on annual average nitrogen fixation rates for a given Fe deposition rate. Nearby measurements of short-term N$_2$-fixation rates exceed our theoretical upper limits, suggesting that N$_2$-fixation in the South Pacific may be episodic, responding to transient Fe supply events.

5.1 Introduction

Wind-blown mineral dust deposition provides a unique source of micronutrients to remote ocean regions, acting as a regulator of global biogeochemistry and elemental cycling in both the modern ocean (Jickells et al. 2005) and in the geologic past (Lamy et al. 2014; Martínez-Garcia et al. 2014). Much of the biogeochemical significance of dust hinges on it being a source of iron (Fe), an element that limits primary productivity in ~30% of the global ocean (Moore et al. 2013). Many other biochemical processes conducted by marine phytoplankton also utilize Fe, most notably nitrogen fixation (Moore et al. 2009), the enzyme (nitrogenase) for which has one of the highest Fe requirements found in nature (Whittaker et al. 2011).

The South Pacific Ocean is a particularly important region for understanding dust and Fe inputs. The South Pacific Gyre (SPG) is among the most oligotrophic oceanic regions, with pervasive nutrient limitation of productivity (Bonnet et al. 2008), the lowest satellite-derived chlorophyll a estimates (e.g. Claustre et al. 2008), and lowest modeled dust inputs
Mahowald et al. (2005) in the ocean. Inverse models have predicted significant N₂-fixation rates for the SPG given the vanishingly low surface nitrate concentrations and proximity to coastal oxygen minimum zones of intense fixed N loss (Deutsch et al. 2007). However, incubation studies typically find much lower N₂-fixation rates in the SPG, a discrepancy that has been attributed to Fe-limitation of diazotrophs (Knapp et al. 2016).

A comprehensive understanding of the feedbacks between dust fluxes, iron input, and biogeochemical processes like N₂-fixation in the South Pacific is still lacking. This is in part because global models of dust input and iron dynamics still have significant uncertainties. Dust deposition models have few observational constraints over the open ocean, particularly in the South Pacific, given its remoteness from the continents and lack of well-dated surface sediments (Albani et al. 2014; Kienast et al. 2016). Different global iron models vary over orders of magnitude in their simulated deposition rates from dust and average water column residence times of dissolved iron (Tagliabue et al. 2016). Observations of modern dust and iron input rates, as well as iron residence times would be of great use in constraining these models, thus improving their ability to simulate biogeochemical feedbacks between iron input and the activity of marine phytoplankton.

Long-lived thorium isotopes in the ocean are highly sensitive tracers of particle flux, and have recently been deployed as tracers of modern dust inputs (Anderson et al. 2016; Deng et al. 2014; Hayes et al. 2013b, 2017; Hsieh et al. 2011; Lopez et al. 2015) and residence times of dissolved trace metals, including Fe (Hayes et al. 2015c, 2018b). While one long-lived Th isotope (²³⁰Th) is produced in the water column at a constant and precisely known rate by ²³⁴U decay, the other (²³²Th) is primordial and brought to the ocean via the dissolution of lithogenic materials. Thorium is extremely particle reactive, and
is rapidly removed from solution by adsorption onto sinking particulate matter (Moore and Sackett 1964). Since it is removed so quickly, it is typically assumed that dissolved 
$^{230}$Th is negligibly redistributed by physical processes, so a 1-d mass budget can be easily constructed between its production by $^{234}$U decay and its removal onto sinking particles (Bacon and Anderson 1982). Applying this 1-d mass budget derived from radiogenic $^{230}$Th to the primordial isotope $^{232}$Th, which shares identical scavenging behavior to $^{230}$Th, allows for the determination of $^{232}$Th (and thus, dust) input rates (Hayes et al. 2013b; Hirose and Sugimura 1987; Hsieh et al. 2011).

In this study we present new high-resolution measurements of dissolved $^{230}$Th and $^{232}$Th from the upper water column, as well as particulate $^{230}$Th and $^{232}$Th measurements, from the South Pacific Ocean between Chile and New Zealand. We first discuss the implications of the dissolved and particulate Th distributions for two different methodologies for determining dust fluxes from water column Th observations. We then use our observations to compute dust input rates, iron fluxes, and iron residence times in the South Pacific, and derive an upper bound of N$_2$-fixation rates that can be supported for a given Fe supply, with implications for diazotrophy in the SPG.

5.2 Materials and Methods

5.2.1 Cruise Track and Sample Selection

Samples were collected aboard the FS Sonne (cruise SO245) on the UltraPac transect between Antofagasta, Chile and Wellington, New Zealand from December 2015-January
2016 (Figure 5.1). Ten-liter samples for dissolved $^{230}\text{Th}$ and $^{232}\text{Th}$ were collected from Niskin bottles deployed on a stainless steel rosette, filtered through 0.45µm Acropak capsule filters into acid-cleaned 10L cubitainers, and immediately acidified to pH=2 using 6M hydrochloric acid. Particulate samples were collected via in-situ filtration using McLane pumps (WTS-LV). Each sample was pumped through a 142-mm-diameter filter holder with a titanium baffle to generate homogenous particle distributions. Samples were collected on paired acid-leached 0.8 µm Pall Supor 800 polyethersulfone filters. Blank filters were deployed along with the pumps on each cast, in a cut-open Ziploc plastic bag zip-tied to the frame of a pump to allow blank filters to be in contact with ambient seawater for the duration of the pump deployment.
5.2.2 Sample Analysis

A 5L aliquot of each 10L dissolved sample was transferred to a new acid-cleaned cubitainer. Spikes of $^{229}$Th and $^{233}$Pa as well as 15 mg of dissolved Fe carrier were added to each sample. The spikes were allowed to equilibrate for 24 hours before sample pH was raised to ~8.5 to precipitate Fe. The resulting Fe precipitate was concentrated, washed in Milli-Q water, and digested at 200°C using concentrated HNO$_3$, HF, and HClO$_4$. Thorium isotopes were then isolated via anion exchange chromatography on Bio-rad AG1-X8 100-200 mesh size resin. Concentrations of $^{230}$Th and $^{232}$Th were measured by isotope dilution using a Thermo ELEMENT XR ICP-MS in peak jumping mode (Anderson et al. 2012).

Procedural blanks for dissolved Th isotopes were determined by processing 3-5L of Milli-Q water in acid-cleaned cubitainers under identical methods. Half the blanks were taken to sea and acidified to pH=2 along with seawater samples, and half the blanks were acidified in the lab. No statistically significant difference was observed between sea blanks and lab blanks processed in this manner. The average of all (n=22) procedural blanks run during the measurement of SO245 samples was used to correct the sample concentrations. Mean and 1σ blanks for dissolved Th isotopes were $^{232}$Th=7.4±5.4 pg and $^{230}$Th=0.47±0.39 fg. Reproducibility was determined by measuring aliquots of two intercalibrated standard solutions of Th isotopes, SW STD 2010-1 (Anderson et al. 2012) and SW STD 2015-1. For standards run alongside SO245 samples, the reproducibility for each isotope was 0.71% for $^{230}$Th and 1.09% for $^{232}$Th on SW STD 2010-1, and was 0.47% for $^{230}$Th and 2.26% for $^{232}$Th on SW STD 2015-1.

Particulate Th isotopes were analyzed similarly to previously described methods
(Pavia et al. 2019a; Pavia et al. 2018). The top 0.8µm Supor filter from each sample was folded into a 60mL Teflon jar, where 229Th and 233Pa spikes, as well as 7-8 mg of dissolved Fe carrier were added. The filters sat overnight at room temperature in 5mL concentrated HNO3, before complete digestion at 220 °C using concentrated HClO4 and HF. After complete dissolution, samples underwent an Fe coprecipitation, the precipitate of which was subsequently washed, re-dissolved, and taken through anion exchange chromatography to isolate Th isotopes. Measurement of particulate 230Th and 232Th concentrations was performed by isotope dilution under similar conditions as dissolved Th concentrations. The pooled average concentration of 232Th and 230Th in all analyzed dipped blank filters (232Th=8.7±4.3 pg, and 230Th=1.6±0.7 fg; n=8) was used to correct measured particulate Th concentrations.

 Corrections were made to both dissolved and particulate data to isolate the 230Th produced by 234U decay in the water column (230Thxs). This includes previously-described (Hayes et al. 2013a; Pavia et al. 2018) corrections to dissolved 230Th for ingrowth during sample storage and for lithogenic contributions. While the corrected 230Thxs data are used for all calculations described in this paper, the subscript xs is henceforth omitted for clarity.

### 5.3 Background: Calculating Dust Fluxes

Two methods have been proposed for determining dust fluxes from water column measurements of thorium isotopes (Anderson et al. 2016). The two methods share some assumptions, namely that the one-dimensional budget for 230Th is a simple mass balance be-
tween $^{234}$U decay and scavenging removal onto particles. However, there are also several assumptions unique to each method. Here, we outline the measurements, calculations, and primary uncertainties involved in determining dust fluxes using thorium isotopes.

### 5.3.1 Dust Fluxes from Dissolved $^{230}$Th-$^{232}$Th

When dust is deposited at the surface ocean, the elements in the lithogenic matrix partially dissolve into solution. For non-bioactive elements with a sufficiently short scavenging residence time to prevent net lateral redistribution, it can be assumed that the upper water column mass budget for these elements reflects a balance between dust dissolution and scavenging removal. By measuring mixed layer concentrations of aluminum (Al), and assuming both a fractional solubility and a scavenging removal rate, early work attempted to exploit this mass budget to calculate dust input rates (Measures and Brown 1996; Measures and Vink 2000).

Like Al, $^{232}$Th is predominantly supplied to the surface ocean of regions far from continental shelves by dust deposition. Unlike Al, there is also a radiogenic isotope of thorium, $^{230}$Th, produced in the water column at a known rate by $^{234}$U decay. Neglecting lateral redistribution, the residence time of Th ($\tau_z$) integrated to depth $z$ can be computed by dividing the water column inventory of $^{230}$Th by its vertically integrated production rate (note that the inventory and production rate are in activity units):

$$\tau_z = \frac{\int_0^z \text{Th}_d \, dz}{\int_0^z \text{234U} \ast \lambda_{230} \, dz} \quad (5.1)$$

Assuming that $^{230}$Th and $^{232}$Th have identical chemical scavenging behavior (e.g. phys-
ical speciation, reactivity), the thorium residence time derived from $^{230}\text{Th}$ can then be applied to $^{232}\text{Th}$ (Hayes et al. 2013b; Hirose and Sugimura 1987; Hsieh et al. 2011). The determination of this residence time circumvents the problems associated with assuming a scavenging residence time for dust flux estimates using Al. Dividing the inventory of dissolved $^{232}\text{Th}$ by the residence time derived from $^{230}\text{Th}$ allows for computation of the $^{232}\text{Th}$ flux:

$$F(\text{Th}) = \frac{\int_0^z \text{Th}_d \, dz}{\tau_z} \quad (5.2)$$

By assuming that the 1-d mass budget of dissolved $^{232}\text{Th}$ reflects a balance between dust dissolution and scavenging removal, the $^{232}\text{Th}$ flux can be converted into a dust flux through dividing by a fractional Th solubility ($S_{\text{Th}}$) and the concentration of $^{232}\text{Th}$ in the dust ($[^{232}\text{Th}]_{\text{dust}}$):

$$\text{Dust Flux} = \frac{F(\text{Th})}{S_{\text{Th}} \cdot [^{232}\text{Th}]_{\text{dust}}} \quad (5.3)$$

### 5.3.2 Dust Fluxes from Particulate $^{230}\text{Th}$-$^{232}\text{Th}$

A second approach to calculate dust fluxes involves measuring $^{230}\text{Th}$ and $^{232}\text{Th}$ on particulate matter in the water column. This method also relies on the assumption that the integrated production of $^{230}\text{Th}$ to depth $z$ by uranium decay is balanced by its removal on particulate matter sinking through that depth. Thus, the $^{230}\text{Th}$ on particulate material is an integration of all the dissolved $^{230}\text{Th}$ produced in the overlying water column. The apparent dust flux at depth $z$ can be calculated by dividing the integrated $^{230}\text{Th}$ production rate by the particulate $^{230}\text{Th}$ concentration at $z$, multiplying by the particulate $^{232}\text{Th}$
Figure 5.2: Upper 500m profiles from SO245. A) Dissolved $^{230}$Th, B) Dissolved $^{232}$Th, C) Chlorophyll fluorescence (WET Labs ECO FL Fluorometer) binned at 1m intervals, D) Turbidity (WET Labs ECO-FL-NTU Turbidity Meter)

dissolved $^{230}$Th concentration at $z$, and dividing by the $^{232}$Th concentration in dust:

$$\text{Dust Flux} = \int_0^z \frac{^{234}U \ast \lambda_{230}}{^{230}\text{Th}} \text{dz} \ast \frac{[^{232}\text{Th}]}{^{230}\text{Th}_dust}$$

(5.4)

5.4 Results

5.4.1 Dissolved and Particulate $^{230}$Th

Dissolved $^{230}$Th ($^{230}$Th$_d$) profiles have constant values of 0.2-0.8 $\mu$Bq/kg in the upper 100-200m, before linearly increasing with depth towards values of 2.5-5 $\mu$Bq/kg at 500m (Figure 5.2a). The depths at which upper water column $^{230}$Th$_d$ remains constant in the uppermost water column vary amongst stations. For stations 2 through 10, depth at which $^{230}$Th begins to increase generally follows the depth of the deep chlorophyll maximum (DCM) at each station, at depths of $\sim$180-200m at stations 4-8 and $\sim$120m at stations 2 and 10. This is consistent with high-resolution $^{230}$Th$_d$ profiles from the upper water column at Station Aloha in the subtropical North Pacific (Hayes et al. 2015c) and subtropical North Atlantic
Figure 5.3: Upper 2000m Th profiles from SO245. A) Dissolved $^{230}$Th, B) Dissolved $^{232}$Th, C) Particulate $^{230}$Th, D) Particulate $^{232}$Th.

(Hayes et al. 2017). This relationship is somewhat more complicated at stations 12-15, furthest west on the SO245 transect. These stations had significantly higher chlorophyll fluorescence at the surface, and high turbidity between the surface and 100m, indicating greater particle abundance and productivity (Figures 5.2c and 5.2d). At station 12, $^{230}$Th$_d$ increases starting at 100m, aligning with the base of the surface-most fluorescence peak, and at stations 14 and 15 $^{230}$Th$_d$ begins increasing at the depth where fluorescence returns to background levels. This pattern was also observed at station 2 of Hayes et al. (2017), which similarly had high surface fluorescence above the DCM.

Between the DCM and 1500m $^{230}$Th$_d$ generally increases linearly with depth (Figure 5.3a), as expected from reversible scavenging (Bacon and Anderson 1982). The slope of this increase with depth varies from station to station, reflecting the integrated scavenging intensity. Stations 12, 14, and 15, with the highest chlorophyll fluorescence and turbidity at the sea surface, reflecting the greatest particle flux, have the lowest $^{230}$Th$_d$ values at 1500m of 7-10 μBq/kg (Figure 5.3a). There is also a gradient between the stations nearest to the South American coast, with $^{230}$Th$_d$ at 1500 m increasing from 13 μBq/kg at station 2 to 16-17 μBq/kg at stations 4, 6, and 8. Like $^{230}$Th$_d$, particulate $^{230}$Th ($^{230}$Th$_p$) tends to
increase linearly with depth between the DCM and 2000m, with values <0.5 μBq/kg at and above the DCM, and values of 1.6-3.4 μBq/kg at 2000m (Figure 5.3c).

5.4.2 Dissolved and Particulate $^{232}$Th

Dissolved $^{232}$Th ($^{232}$Th$_{d}$) at stations 4-10 show consistent profile shapes with constant, low $^{232}$Th of 0.002-0.01 pmol/kg in the upper 300m increasing to 0.15-0.3 pmol/kg at 500m (Figure 5.2b). These surface $^{232}$Th$_{d}$ concentrations are 4-10 times lower than at the surface of Station Aloha in the subtropical North Pacific (Hayes et al. 2015c). At station 2, $^{232}$Th$_{d}$ is also ~0.005 pmol/kg in the upper 120m, then steadily increases towards 0.03 pmol/kg between 120m-500m (Figure 5.2b). Like for $^{230}$Th$_{d}$, stations 12-15 have much different $^{232}$Th profiles. Except for a single high $^{232}$Th$_{d}$ value of 0.02 pmol/kg at 20m, $^{232}$Th$_{d}$ at station 12 is constant at ~0.01 pmol/kg from 0-150m, then increases linearly below 150m to 0.06 pmol/kg at 500m. Station 14 has variable $^{232}$Th$_{d}$ between 0.01 and 0.03 pmol/kg in the upper 150m, then increases towards a maximum of 0.11 pmol/kg at 250m, before reaching constant values of 0.08-0.09 pmol/kg from 250m-500m. Station 15 has similarly high $^{232}$Th$_{d}$ of 0.025 pmol/kg in the upper 50m, then increases sharply towards a broad maximum of 0.22 pmol/kg between 150m and 250m, before decreasing to 0.13 pmol/kg at 500m.

Below 500m, $^{232}$Th$_{d}$ at stations 2-8 continues to increase with depth, reaching peak values of 0.035 pmol/kg at 750m before decreasing to 0.02 pmol/kg at 1500m (Figure 5.3b). At stations 10 and 12, the $^{232}$Th$_{d}$ values at 750m are higher, at 0.055 pmol/kg and 0.075 pmol/kg respectively, and remain roughly constant to 1500m. The $^{232}$Th$_{d}$ at station 14
increases from 0.08 pmol/kg at 300m to 0.09 pmol/kg at 750-1000m, before decreasing to 0.06 pmol/kg at 1500m. At station 15, $^{232}\text{Th}_d$ decreases from its maximum value of 0.22 pmol/kg at 250m to a constant value of 0.09 pmol/kg between 750m and 1500m.

Particulate $^{232}\text{Th}$ ($^{232}\text{Th}_p$) decreases slightly from the surface to the DCM at all of stations 2-10, with values of 0.4-2.3 fmol/kg at 20m, and 0.24-0.6 fmol/kg at the DCM (Figure 5.3d). The $^{232}\text{Th}_p$ at each of these stations then increases to constant values of 2-7 fmol/kg at 1000m-2000m. Highest $^{232}\text{Th}_p$ between stations 2-10 is found at stations 2 and 10, followed by station 4, with the lowest concentrations found at stations 6 and 8. At station 12 $^{232}\text{Th}_p$ increases from 0.67 fmol/kg at the surface to 9.6 fmol/kg at 2000m, while at station 14 there is a subsurface $^{232}\text{Th}_p$ maximum of 13.3 fmol/kg at 250m. Station 15 was the only location where a high-resolution profile of particulate Th isotopes was collected. Here, the highest surface $^{232}\text{Th}_p$ concentrations of the entire transect were observed at 11 fmol/kg. Concentrations increased to 43.8 fmol/kg at 100m, increasing further to 52.8 fmol/kg at 500m, then increasing steeply to 150 fmol/kg between 500m and 1000m.

5.5 Discussion

5.5.1 Depth-Dependence of Thorium Residence Times and Dust Fluxes

5.5.1.1 Shallow Dissolved $^{230}\text{Th}$ dynamics

Depth-integrated residence times for thorium ($\tau$) are computed using Equation 5.1. The depth profile of $\tau$ follows the same pattern at each station (Figure 5.4a) as the depth pat-
tern of $^{230}\text{Th}_\text{d}$ (Figure 5.2a). Near-surface $\tau$ is 0.5-2 years, is constant with depth in the upper 100-200m, then increases linearly with depth down to 500m (Figure 5.4a). There are also vertical trends in profiles of depth-integrated dissolved $^{232}\text{Th}$ flux computed using Equation 5.2 (5.4b). If both dissolved Th isotopes were scavenged with uniform and consistent rate constants throughout the water column, and if $^{232}\text{Th}_\text{d}$ were only supplied at the sea surface by dust dissolution, then vertical profiles of dissolved $^{232}\text{Th}$ flux would be constant with depth, as required by mass balance.

The depth-dependence of $^{232}\text{Th}$ flux profiles introduces complications for comparing dissolved thorium-derived dust fluxes with estimates from other methods and models, as an integration depth must be chosen as representative of the true dust flux. Which integration depth is right? It is impossible to determine the proper integration depth a priori. Previous studies have chosen a variety of different options. Hsieh et al. (2011) only integrated within the mixed layer ($\sim$25m) to avoid possible complications from lateral advection of non-local $^{232}\text{Th}$ in the shallow subsurface. Hayes et al. (2013b) and Lopez et al.
(2015) chose 500m to average any seasonal variability in $^{232}\text{Th}$ deposition and reduce possible uncertainties associated with vertical transport of $^{230}\text{Th}$ into the mixed layer. More recent studies have argued for an intermediate approach of using 250m (Deng et al. 2014), or the base of the euphotic zone or DCM (Hayes et al. 2017).

The choice of integration depth would ideally not be subjective, but based on objective criteria derived from an understanding of the mechanisms that drive increasing $^{232}\text{Th}$ fluxes with depth. The physical and biogeochemical processes involved in the shallow (<500m) cycling of $^{230}\text{Th}$ and $^{232}\text{Th}$ remain somewhat poorly understood, in part because thorium profiles with high vertical resolution in the upper 500m remain sparse. At a basic level, trends in $^{232}\text{Th}$ flux as a function of integration depth are governed by the relative depth rate of change in residence time $\tau$ vs. $^{232}\text{Th}$ inventory (see Equation 5.2). Increasing $^{232}\text{Th}$ flux with depth implies that growth of $^{232}\text{Th}$ inventories outpaces increases in $\tau$.

Several mechanisms have been put forward to explain increasing apparent dissolved $^{232}\text{Th}$ fluxes with depth. One, that $^{232}\text{Th}$ is preferentially bound in rapidly-cycled colloids compared to $^{230}\text{Th}$, has largely been ruled out on the basis of similar fractions of colloidal $^{230}\text{Th}$ and $^{232}\text{Th}$ between the surface and 1000m, albeit with limited data to date (Hayes et al. 2015c, 2017). More recently, Hayes et al. (2017) suggested that rapid, non-reversible $^{230}\text{Th}$ removal coincident with particulate organic carbon export from the euphotic zone could explain the constant $\tau$ and increasing $^{232}\text{Th}$ flux from the surface to the DCM in the subtropical North Atlantic. Were this the case, the $^{230}\text{Th}$ inventory down to the DCM would underrepresent the true residence time, causing an underestimation of the $^{232}\text{Th}$ flux.

We contend that the hypothesis of Hayes et al. (2017) is generally correct, but that dif-
different biogeochemical dynamics are responsible for the phenomenon of rapid $^{230}$Th export from the euphotic zone in highly oligotrophic regions and more productive regions. As described in section 5.4.1, $^{230}$Th$_d$ stays constant through the depth of the fluorescence maximum at oligotrophic locations: SO245 stations 2-10, Station Aloha (Hayes et al. 2015c), and stations 6 and 8 from AE1410 in the subtropical North Atlantic (Hayes et al. 2017). At more productive stations with higher surface fluorescence and/or turbidity (SO245 stations 12, 14, and 15 and AE1410 Station 2), $^{230}$Th$_d$ increases very slightly with depth through the base of the DCM rather than staying constant. While the increase is slight, it is consistent with a particle dynamics mechanism for $^{230}$Th export, i.e. reversible scavenging onto fast-particles sinking through the euphotic zone. The presence of fast-sinking particles at these stations is qualitatively supported by the high-frequency of spikes in the turbidity profiles, which are related to the transient presence of large particles (e.g. Gardner et al. 2000; Ohnemus et al. 2018).

At the oligotrophic stations, there are no turbidity spikes indicative of the presence of large particles, and phytoplankton communities above the DCM in the SPG are generally dominated by small picoplankton taxa such as Prochlorococcus and SAR11 (Reintjes et al. 2019; Walsh et al. 2015). The constancy of the $^{230}$Th profiles through the DCM at stations 2-10 suggest a different mechanism at play than at stations 12-15, where the profiles are steeply sloped but not constant. We suggest that these profiles at Stations 2-10 reflect steady-state particle export in the SPG by the diel vertical migration (DVM) of zooplankton. Previous studies have found that zooplankton respiration rates reach 50% of primary production rates in the SPG (Carlotti et al. 2018). Whereas particle sinking quickly through the water column would allow for $^{230}$Th exchange between solid and so-
lution, particle packaging in the euphotic zone by zooplankton and subsequent export at depth circumvents $^{230}$Th exchange between the depth of consumption and excretion. This process would drive steady state removal of $^{230}$Th and constant $^{230}$Th$_d$ profiles at the depths in the euphotic zone where zooplankton feed.

5.5.1.2 Shallow Dissolved $^{232}$Th dynamics and the Ultimate Choice of Integration Depth

Another potential way for $^{232}$Th fluxes to increase with depth is if there is a laterally-advected source of $^{232}$Th in subsurface waters. These waters could be transported from regions of higher dust flux, or could have been in recent contact with shallow continental margin sediments. Constant $^{232}$Th$_d$ in the upper 300m at stations 4-10 argues against a laterally-transported $^{232}$Th source in the shallow subsurface at these stations. This suggests that the increase in $^{232}$Th flux with depth in the upper 200m of these stations reflects rapid $^{230}$Th export as described in section 5.5.1.1, and that the constant $^{232}$Th flux between 200m and 300m at these stations reflects the “true” depth-integrated $^{232}$Th flux without artifacts. While stations 2 and 12 have increasing $^{232}$Th$_d$ below 150m, the depth-integrated $^{232}$Th flux remains constant within error from 150m-250m. Thus, for stations 2-12 we argue that integrating to 250m generates reasonable, internally consistent estimates of $^{232}$Th flux (and thus dust flux) that can be compared across the transect.

At stations 14 and 15, there is a sharp increase in $^{232}$Th$_d$ coincident with an increase in $^{232}$Th flux between the surface and 250m. Below 250m, the $^{232}$Th$_d$ concentrations at both stations decrease and converge towards $\sim$0.08 pmol/kg at 800m. The $^{232}$Th fluxes are constant at each station from $\sim$350-500m. Assuming that these subsurface $^{232}$Th maxima are
not locally-sourced from atmospheric deposition, \(^{232}\)Th fluxes below the depth at which non-local \(^{232}\)Th is introduced will overestimate dust supply. We will use the 250m integration depth for calculating dust fluxes at stations 14 and 15, while noting that these are likely overestimations.

5.5.1.3 Particulate \(^{230}\)Th-Normalized \(^{232}\)Th Fluxes and Depth Choices

Like for dissolved \(^{232}\)Th fluxes, there is also depth variability in particulate \(^{230}\)Th-normalized \(^{232}\)Th fluxes. Fluxes computed by this method increase in the upper 1000m, and are constant from 1000-2000m (Figure 5.5). A similar pattern has been observed in the North Atlantic, both in particulate \(^{232}\)Th fluxes (Hayes et al. 2018a) and in sediment traps (Huang and Conte 2009) near the Bermuda Atlantic Time Series, attributed to lateral transport of lithogenic material from continental margins in the western Atlantic.
Increasing $^{230}$Th$_p$-normalized $^{232}$Th fluxes are also observed in the central North Atlantic, too far from coastal margins for lateral sediment transport to be important (Anderson et al. 2016). This was hypothesized to be due to rapid export of fine lithogenic particles from the upper water column in large aggregates, which subsequently disaggregate throughout the thermocline (Ohnemus and Lam 2015).

On SO245, the particles collected by *in-situ* filtration were not size fractionated as on the North Atlantic GEOTRACES section, so the particulate $^{232}$Th fluxes reflect both fine and coarse particulate material. If the export-disaggregation mechanism used to explain increasing $^{232}$Th$_p$ fluxes in the North Atlantic were occurring in the South Pacific as well, it would require that the particle aggregates responsible were too large and/or fast-sinking to be collected by *in-situ* filtration. This would also imply that there is a particle class either not collected or undercollected by *in-situ* filtration that is important for water column thorium cycling. Future measurements of thorium isotope concentrations in large particles, including those collected by sediment traps, may improve our understanding of the processes that generate these features. Regardless, given the constancy of $^{230}$Th$_p$-normalized $^{232}$Th$_p$ fluxes below 1000m and uncertainties regarding the upper water column dynamics of $^{232}$Th$_p$, we use $^{232}$Th$_p$ fluxes from 1000m as representative for computing dust fluxes from this method.
5.5.2 Dust Fluxes from Dissolved and Particulate $^{230}$Th-$^{232}$Th in the South Pacific

Having established the depths to use for calculating dust fluxes from dissolved (250m) and particulate (1000m) $^{230}$Th-$^{232}$Th measurements, we now compare our estimates of dust flux between the two methods, with model estimates of dust deposition in the SPG, and with a compilation of $^{230}$Th-normalized dust fluxes from surface sediments in the Pacific.

Two additional variables must be defined for converting $^{232}$Th fluxes for dust fluxes. In both the dissolved and particulate methods, the concentration of $^{232}$Th in dust ($[^{232}\text{Th}]_{\text{dust}}$) is used to convert from calculated $^{232}$Th fluxes to dust fluxes. The likely source regions for the entirety of the SO245 transect, western South America and Australia, have similar $^{232}$Th concentrations of 14±1 ppm in fine (<5 μm) fractions of sediments from likely dust source areas (McGee et al. 2016), and we adopt this value and its uncertainty for $[^{232}\text{Th}]_{\text{dust}}$. For dust fluxes from dissolved $^{230}$Th-$^{232}$Th, the fractional solubility of thorium ($S_{\text{th}}$) is an additional variable that must be assigned. $S_{\text{th}}$ remains poorly constrained, with a lower bound of 1% and an upper bound of 28% (Arraes-Mescoff et al. 2001; Hayes et al. 2013b, 2017; Hsieh et al. 2011; Roy-Barman et al. 2002). We adopt the most-recent estimate from of $S_{\text{th}}=0.21±0.07$ derived from comparing aerosol settling fluxes of $^{232}$Th with 250m-integrated $^{232}$Th$_d$ fluxes from the North Atlantic (Hayes et al. 2017). For estimates of dust flux from particulate $^{230}$Th-$^{232}$Th, we also introduce a nominal 30% uncertainty typically assigned to the assumption that $^{230}$Th flux through a depth horizon is equal to its water column production rate (Henderson et al. 1999).

Despite the numerous caveats associated with both methods employed here for de-
Figure 5.6: Observed and modeled dust fluxes at each station on the SO245 transect. Dissolved estimates of dust fluxes use 250m integration depths and parameters described for calculating dust flux in Figure 4.5. Particulate estimates of dust flux were taken from 1000m depth as described in section 5.5.1.3. Modeled dust deposition rates from the nearest grid cell to sampling stations were extracted from CAM3 (Mahowald et al. 2006), and three separate model setups for CAM4 and CAM5 also described in section 5.5.2 (Albani et al. 2014).

termining dust flux, we find strong agreement between the two methods for most of the SO245 section. At seven of eight stations, dust fluxes from the two methods are within 1-sigma uncertainty (Figure 5.6). Dust fluxes from the two methods also follow a similar zonal pattern, decreasing westward from station 2 toward station 6, and increasing westward from station 10 to station 15. Increasing fluxes at the furthest east and west ends of the section suggest that both Australia and South America serve as dust sources to the SPG.

Though the methods agree within stated uncertainties and show the same spatial pattern of dust flux in the South Pacific, there are consistent offsets observed between the two methods. Dust fluxes from the dissolved method are always higher than those from the particulate method. One possibility is that we have underestimated the solubility of Th -
greater $S_{\text{Th}}$ would decrease the dust flux estimates from dissolved Th isotopes. However, if the solubility of Th were the only reason for the discrepancy, the dissolved Th estimates of dust fluxes should be offset higher than particulate estimates by a constant factor, reflecting the factor by which $S_{\text{Th}}$ has been overestimated. Instead, with the exception of station 14, we observe a zonal trend in the factor by which dissolved Th-based dust fluxes are higher. The dissolved Th dust estimates are 2.1-2.3 times greater at stations 2 and 4, decreasing monotonically to be 1.2 times greater at station 12, before increasing to be 1.6 times greater at station 15.

Regardless of the differences between our two methods, the consistency and reproducible spatial pattern of dust fluxes we have calculated provide valuable benchmarks for models of dust deposition to the open ocean. Few observations of dust flux are available to calibrate dust models over remote ocean regions like the SPG. The observations that exist typically rely on aerosol measurements and assumptions of settling velocities (dry deposition) and scavenging efficiency by precipitation (wet deposition). These aerosol-based estimates of dust flux also only provide a snapshot, integrated on weekly to monthly timescales. One such estimate from the SPG gave dust deposition rates 0.002-0.007 g/m$^2$/yr, a full order of magnitude lower than our observations from thorium isotopes (Wagener et al. 2008). This discrepancy may be due to seasonality, which is important for dust emissions from Australia and South America (Mackie et al. 2008) with Th isotopes integrating across large dust deposition events missed during the timescales of aerosol sampling.

The dust input rates we calculate for the SPG are the lowest tracer-based estimates of dust flux observed to date in the world ocean. At SO245 stations 4 and 6, we find
dust deposition rates of 0.02-0.05 g/m²/yr. These are an order of magnitude lower than dissolved Th-based estimates of dust flux in the Equatorial Pacific (Lopez et al. 2015) and subtropical North Pacific (Hayes et al. 2013b), nearly two orders of magnitude lower than in the subpolar North Pacific (Hayes et al. 2013b), and two-three orders of magnitude lower than in the subtropical North Atlantic (Anderson et al. 2016; Hsieh et al. 2011). Many more reconstructions of late-Holocene dust flux are available from surface sediment measurements of Th isotopes, compiled recently in the Thoromap database (Kienast et al. 2016). The lowest dust fluxes in the Thoromap database, from the Eastern Equatorial Pacific, are 2-4 times higher than those we measure at SO245 stations 4 and 6.

We compare our estimates with those from four realizations of dust models from the Community Earth System Model’s Community Atmosphere Model (CAM): one from CAM3 using a slab ocean model and land model vegetation (CAM3 TIMIND (Mahowald et al. 2006)) one from the Community Atmosphere Model version 4 (CAM4) with model winds (C4fn), one from CAM4 with reanalysis winds (C4wn), and from Community Atmosphere Model version 5 (CAM5) with reanalysis winds (C5wn). CAM4 and CAM5 model results are from Albani et al. (2014) The older CAM3 model is in much better agreement with our results from thorium isotopes in the eastern part of the SO245 section while CAM4 and CAM5 dust models underestimate thorium-derived dust fluxes by 1-2 orders of magnitude (Figure 5.6). The disagreement between models and observations is greatest in the eastern portion of the transect, suggestive of the models missing a South American dust source carried to the SPG by easterly trade winds. The broad model-data disagreement is consistent with previously noted model underestimation of Southern Hemisphere dust deposition compared to terrestrial archives (Albani et al. 2014). Given the extreme
paucity of other measurements of Holocene dust fluxes in the South Pacific Ocean which could be used to validate model estimates (Kienast et al. 2016), we recommend caution when using modeled dust deposition to derive input rates of micronutrients like Fe to the South Pacific.

5.5.3 Iron Input Rates and Residence Times

The South Pacific Gyre is an important location for diagnosing dust-borne Fe fluxes. There have been significant mismatches between models (Deutsch et al. 2007) and observations (Knapp et al. 2016) of nitrogen fixation rates in the SE Pacific, hypothesized to be due in part to the inability of models to properly account for iron-limitation. Diazotrophs have much greater cellular Fe quotas than other phytoplankton types (Berman-Frank et al. 2001), due in part to the high Fe requirements of the nitrogenase enzymes used in nitrogen fixation (Raven 1988; Whittaker et al. 2011). Quantifying iron fluxes from dust deposition across the South Pacific Gyre would be a critical step towards determining how much nitrogen fixation can take place in different regions and resolving model-data discrepancies in the spatial distribution of nitrogen fixation in the South Pacific.

Fluxes of soluble trace elements (here, Fe) can be determined from dissolved thorium isotopes via a modified form of Equation 5.3:

\[
\text{Dissolved Fe Flux} = F^{(232\text{Th})} \times \left[ \frac{\text{Fe}}{232\text{Th}} \right]_{\text{dust}} \times \frac{S_{\text{Fe}}}{S_{\text{Th}}} \tag{5.5}
\]

Rather than an absolute solubility, this requires knowledge of the fractional solubility ratio of Fe to Th, \(S_{\text{Fe}}/S_{\text{Th}}\). There is significant variance across different leaching-based
methods for determining the absolute solubility of Th and Fe in aerosols (Anderson et al. 2016). However, the relative solubility of Fe to Th is better-established, with time-series observations of $^{232}$Th and Fe in the surface ocean at Station Aloha suggesting $S_{Fe}/S_{Th}$ is close to 1 (Hayes et al. 2015c), and acetic acid leaching of African dust samples produced $S_{Fe}/S_{Th}$ of 1.3±0.3 (Hayes et al. 2018b). Another plausible approach is to measure concentrations of acetic acid-soluble trace elements in aerosols from dust source areas supplying the study area. If concentrations of both soluble iron and thorium are measured in aerosols, the ratio of aerosol soluble Fe/Th (here denoted [Fe/Th]$_{sol}$) should reflect the product of [Fe/Th]$_{dust}$ multiplied by $S_{Fe}/S_{Th}$. Baker et al. (2016) performed these measurements off the coast of Peru between 6-16ºS, just to the north of the easternmost stations in our study area, finding [Fe/Th]$_{sol}$ of 6220±1990 mole/mole. The 5-day air mass back trajectories from the sites of Baker et al. (2016) lead to nearby our station 2, suggesting that [Fe/Th]$_{sol}$=6220±1990 is also indicative of the aerosols being deposited at our eastern-most stations on SO245. However, this is 3.25 three times lower than the [Fe/Th]$_{sol}$=20215±4665 derived by multiplying Fe/Th ratio in average upper continental crust (15,500 mole/mole) by $S_{Fe}/S_{Th}$=1.3±0.3. Since we do not know the absolute value of [Fe/Th]$_{sol}$, we can only estimate iron inputs rates, and thus residence times, within this factor of 3.25.

We find soluble Fe fluxes, integrated to 250m, of 7-23 μmol m$^{-2}$ yr$^{-1}$ at station 2, decreasing to 3.5-11 μmol m$^{-2}$ yr$^{-1}$ at stations 4-10 in the center of the SPG, before increasing towards 114-370 μmol m$^{-2}$ yr$^{-1}$ at station 15 (Table 1). The dust-borne Fe fluxes to the SPG we derive using Equation 5.5 are comparable to one recent dust Fe flux estimate of 8.7 μmol m$^{-2}$ yr$^{-1}$ from aerosol measurements (Buck et al. 2013). Another aerosol-based estimate of soluble iron to the SPG of 2.2-3.7 μmol m$^{-2}$ yr$^{-1}$ (Wagener et al. 2008)
Table 5.1: Fe fluxes and residence times at each SO245 station. Fe fluxes were calculated using Equation 5.5, integrated to 250m. Residence times are similarly integrated to 250m, calculated using Equation 5.6, with dFe inventories at SO245 stations 2 and 4 coming from stations 4 and 7 from Fitzsimmons et al. 2016, and the dFe inventory at SO245 station 8 coming from station GYR from Blain et al. 2008. The values given for dFe residence times reflect calculations using North American aerosol $S_{Fe}/S_{Th}$ (lower residence time) vs. the $S_{Fe}/S_{Th}$ ratio from Baker et al. 2016 (higher residence time).

<table>
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<tr>
<th>Stn</th>
<th>Lat</th>
<th>Lon</th>
<th>dFe dust flux (Aerosol Ratio) μmol m⁻² d⁻¹</th>
<th>dFe dust flux (Baker Ratio) μmol m⁻² d⁻¹</th>
<th>dFe vertical flux μmol m⁻² d⁻¹</th>
<th>dFe Inventory μmol m⁻²</th>
<th>$\tau_{Fe}$</th>
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<td>-100</td>
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<td>2.3</td>
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</tbody>
</table>

is ~3 times lower than our fluxes using [Fe/Th]_{sol} of mineral aerosols, but very similar to our fluxes determined using [Fe/Th]_{sol} from Baker et al. (2016). Fewer comparisons exist for the western portion of the transect. Based on rainwater Fe concentrations and an assumed annual precipitation rate at 32.5°S and 170°W, Ellwood et al. (2018) estimated dust Fe fluxes of 26.3 μmol m⁻² yr⁻¹, about 5-10 times lower than our estimate of 114-370 μmol m⁻² yr⁻¹ at station 15. This discrepancy may indicate that a substantial portion of the dFe flux integrated to 250m we compute at station 15 is derived from lateral transport of lithogensics dissolved on the Chatham Rise.

Where there are depth profiles of dissolved Fe coincident with Th-based estimates of dFe input rates, the residence time of iron can be determined by dividing the dissolved
inventory at a given depth by the dissolved flux integrated to that depth determined from Equation 5.5:

$$\tau_{Fe} = \frac{I_{Fe}}{dFe \text{ Flux}}$$ (5.6)

While there were no measurements of dFe made on the SO245 cruise, there are published dFe profiles from within ~400km of stations 2, 4, and 8. Dissolved Fe data collected at stations 4 and 7 from the BiG RAPA transect (Fitzsimmons et al. 2016) can be combined with Fe fluxes from SO245 stations 2 and 4, respectively, and dFe profiles from the BIOSOPE GYR station (Blain et al. 2008) can be combined with Fe fluxes from SO245 station 8. Calculating residence times of Fe from dFe fluxes derived from Th isotopes assumes that dust-borne Fe constitutes the primary Fe source at a given location. Fitzsimmons et al. (2016) argued that lateral diffusive fluxes of Fe from the South American shelf constituted the largest dFe source to the upper 250m of the SPG by several orders of magnitude. However, their method (also used by Rijkenberg et al. (2012)) for calculating lateral diffusive Fe fluxes makes several unjustifiable assumptions that warrant discussion. A conceptual error in these estimates and those of Labatut et al. (2014) is comparing vertical fluxes through a horizontal plane at a reference depth with lateral fluxes through a vertical plane parallel to the coast. A significant portion of this lateral flux could simply be transported further offshore. Rather than the lateral flux in, it is necessary to compute the convergence of lateral flux (i.e. the second derivative $d^2[\text{dFe}] / dx^2$) to determine whether there is a net dFe supply at each station studied. Using only the input (output) flux terms to compute residence times, rather than the flux convergence, will result in a substantial overestimation of supply (removal) rates, and underestimation of residence times.
Figure 5.7: Profiles of dissolved Fe from Fitzsimmons et al. (2016) plotted against potential density ($\sigma_f$).
We revisit the dFe gradients of Fitzsimmons et al. (2016) and show that far less Fe can be transported to the upper 250m of the SPG by isopycnal mixing of coastal Fe than was inferred by Fitzsimmons et al. Near the South American continent, wind-driven upwelling brings deeper isopycnal layers close to the surface. The ferricline in the SPG observed by Fitzsimmons et al. (2016) was found below the potential density surface $\sigma = 26.0 \text{ kg/m}^3$ (Figure 5.7). The calculated dFe gradients both for deriving an apparent lateral diffusivity and for determining lateral fluxes in Fitzsimmons et al. (2016) were determined between the depth of the mixed layer and 250m at each station. Because of the shoaling density layers near the South American continent, the dFe inventories at these stations encompass substantially different density layers: closer to the continent this integrates to potential densities up to $\sigma = 26.6 \text{ kg/m}^3$. Furthermore, the vast majority of the high dFe concentrations near the continent is found at these denser layers, with density greater than $\sigma = 26.0 \text{ kg/m}^3$ (Figure 5.7). There are negligible offshore dFe gradients at densities above $\sigma = 26.0 \text{ kg/m}^3$ (Figure 5.7), indicating that there cannot be substantial offshore transport of dFe by isopycnal mixing at lighter densities than this. At the offshore stations 4-7, since $\sigma = 26.0 \text{ kg/m}^3$ is found at $\sim 250m$, this implies minimal transport of dFe by lateral mixing into the upper 250m. Dissolved Fe inventories integrated to the $\sigma = 26.0 \text{ kg/m}^3$ density horizon at each station from Fitzsimmons et al. (2016) actually increase moving offshore, due to the much shallower depth of the $\sigma = 26.0 \text{ kg/m}^3$ isopycnal nearshore (Figure 5.8). While there is a concentration gradient moving offshore at $\sigma = 26.0 \text{ kg/m}^3$, mixing will act to transport dFe along this isopycnal. By station 4, this isopycnal is at 250m, the upper depth of the ferricline (Figure 5.8), indicating that lateral mixing will act to transport dFe at or below the upper 250m, not within the upper 250m. The correlation between dFe and AOU below
Figure 5.8: Characteristics of dissolved iron and physical setting from Southeast Pacific data of Fitzsimmons et al. (2016). Iron concentration at each station was linearly interpolated onto the $\sigma=26.0$ isopycnal, as was isopycnal depth. Red dots show dissolved Fe inventories integrated to the depth of $\sigma=26.0 \text{ kg/m}^3$. Blue squares show the dissolved Fe concentration at $\sigma=26.0 \text{ kg/m}^3$. Black triangles show depth of the $\sigma=26.0 \text{ kg/m}^3$ isopycnal.

250m (or $\sigma=26.0 \text{ kg/m}^3$) in the SPG is likely due to the shared influence of diffusive mixing in transporting low-O$_2$ high-Fe waters from the continental shelf into the SPG at depth, rather than regeneration of Fe from above.

Since lateral mixing cannot supply substantial dFe to the upper 250m of the SPG, the two remaining Fe fluxes important for computing $\tau_{\text{Fe}}$ are dust input and vertical mixing from below. Using diffusivity estimates from CTD profiles of vertical density gradients Fitzsimmons et al. (2016) calculate vertical diffusive Fe supply rates of 2.1 $\mu\text{mol m}^{-2} \text{ yr}^{-1}$
and 2.3 μmol m$^{-2}$ yr$^{-1}$ at 250m for BiG RAPA stations 4 (SO245 station 2) and 7 (SO245 station 4) respectively. We note that these vertical diffusive dFe supply rates are a factor of 2-10 lower than the input rates we compute from dust input, suggesting that atmospheric deposition is the most important supply term of Fe to the SPG. No vertical dFe gradient was observed by Blain et al. (2008) in the upper 400m at the BIOSOPE GYR station (SO245 station 8), so a vertical supply term is not included in the \( \tau_{Fe} \) calculation here.

We compute \( \tau_{Fe} \) using Equation 5.6, with \( I_{Fe} \) integrated to 250m, using the sum of the vertical diffusive inputs as calculated in Fitzsimmons et al. (2016) and Th-based atmospheric dFe input rates (calculated using Equation 5.5, integrating to 250m) for dFe Flux. The Fe residence times increase moving offshore, from 0.75-2 years at station 2, to 1.2-2.8 years at station 4, to 1.8-4.4 years at station 8 (Table 1). These values are similar to the residence times of 0.5-1 years observed at 250m at Station Aloha derived from the same method (Hayes et al. 2015c) and 2-5 times longer than 250m estimates from the North Atlantic (Hayes et al. 2018b), but shorter than the residence time of dFe in the mixed layer inferred from the Southwest Pacific (Ellwood et al. 2018). Shorter iron residence times near the edge of the SPG compared to the center is consistent with iron addition experiments from BIOSOPE suggesting Fe limitation of photoautotrophs only at the edges of the SPG, but not in the center (Bonnet et al. 2008).

5.5.4 Biogeochemical Implications for Diazotrophy

We can also place an uppermost limit on the amount of N$_2$-fixation that can be supported by a given amount of Fe flux from dust. Our approach is based on elemental quotas
measured in trichodesmium. We interpret our maximum N$_2$-fixation rates while mindful that heterotrophs like unicellular Group A cyanobacteria (UCYN-A) (Halm et al. 2012) or gammaproteobacteria (Moisander et al. 2014) may be responsible for the majority of diazotrophy in the SPG. We use estimates of dust flux from Equation 5.3 multiplied by 3.5 wt% Fe in upper continental crust (Rudnick and Gao 2014) to determine a bulk iron supply from dust (e.g. not just soluble Fe, but all Fe). This term can be multiplied by a fractional bioavailability of Fe in dust, $f_{bio}$, to calculate the input of bioavailable iron from dust deposition $F_{Fe,bio}$:

$$F_{Fe,bio} = \text{Dust Flux} * [\text{Fe}]_{UCC} * f_{bio} \quad (5.7)$$

Typically, $f_{bio}$ would be assumed to be equal to the solubility of Fe. However, Trichodesmium and its epibiont are capable of solubilizing and accessing particulate Fe in dust particles (Rubin et al. 2011). In the spirit of deriving an upper-limit on N$_2$-fixation rates possible from our derived Fe input rates from dust, we leave $f_{bio}$ equal to 1 and assume that all Fe deposited by dust to the surface ocean is bioavailable. Given that bacteria like UCYN-A likely do not form the filamentous colonies that allow Trichodesmium to capture and solubilize dust particles, the true value for $f_{bio}$ in the SPG may be far lower, close to the fractional solubility of Fe in dust. Trichodesmium require 236 µmol Fe in nitrogenase per mole cellular C (Whittaker et al. 2011), and have a cellular C:N ratio of 6.03±1.05 mole/mole (Nuester et al. 2012). By assuming that every atom of new Fe supplied is bound in the nitrogenase enzyme of Trichodesmium, and every atom of cellular N has been fixed from N$_2$, we can calculate an upper bound N$_2$-fixation rates for a given
Fe supply rate:

\[ N_{\text{fix}}^{\text{max}} = F_{\text{Fe, bio}} \times \frac{1 \text{ mole cellular C}}{236 \mu \text{mol N in nitrogenase}} \times \frac{1 \text{ mole cellular N}}{6.03 \text{ moles cellular C}} \]  

(5.8)

We find \( N_{\text{fix}}^{\text{max}} \) values as low as 50-65 \( \mu \text{mol N m}^{-2} \text{ d}^{-1} \) in the center of the SPG at stations 4-10 (Figure 5.9). Since the dissolved Th-based estimates of dust flux from which Fe fluxes are derived integrate across 1-2 year timescales (i.e. the upper water column residence time of \( ^{230}\text{Th} \)), so too do our estimates of \( N_{\text{fix}}^{\text{max}} \). These estimates of \( N_{\text{fix}}^{\text{max}} \) may be useful for comparing with model fields of \( \text{N}_2 \)-fixation, as steady-state modeled \( \text{N}_2 \)-fixation rates should not exceed the maximum amount allowed by Fe supply.

Direct comparison of our \( N_{\text{fix}}^{\text{max}} \) estimates with observations of \( \text{N}_2 \)-fixation rates is complex, since measurements of \( \text{N}_2 \)-fixation rates are typically performed using shipboard incubations lasting <24 hours (e.g. Montoya et al. 1996). Measurements of \( \text{N}_2 \)-fixation rates at 20ºS from 80-100ºW just north of SO245 stations 2 and 4, occasionally exceeded long-term \( N_{\text{fix}}^{\text{max}} \), reaching 98 \( \mu \text{mol N m}^{-2} \text{ d}^{-1} \) at 100ºW compared to \( N_{\text{fix}}^{\text{max}} \) of 65 \( \mu \text{mol N m}^{-2} \text{ d}^{-1} \) (Knapp et al. 2016). \( \text{N}_2 \)-fixation rates measured at the same location as SO245 station 8 also exceeded our derived there (Halm et al. 2012). Rates of \( \text{N}_2 \)-fixation made in separate years in the ETSP varied substantially between years, suggesting that there is temporal variability in diazotrophy in the region (Dekaezemacker et al. 2013; Knapp et al. 2016). We suggest that \( \text{N}_2 \)-fixation rates above \( N_{\text{fix}}^{\text{max}} \) reflect a response to episodic dust supply events, which deposit Fe to the surface ocean at rates above the long-term average, allowing for short-term \( \text{N}_2 \)-fixation rates greater than \( N_{\text{fix}}^{\text{max}} \). This effect has been suggested for the Atlantic (Mills et al. 2004), observed in unicellular diazotrophs in the Tasman Sea.
Figure 5.9: Maximum theoretical $N_2$-fixation rates possible for a given iron input rate from dust at each station calculated using Equations 5.7 and 5.8. Dust flux estimates derived from dissolved Th isotopes at 250m were used in the calculations.
following a cyclone (Law et al. 2011) and seasonal changes in N\(_2\)-fixation in the western North Pacific (Kitajima et al. 2009), and modeled to be important in parts of the SE Pacific (Guieu et al. 2014). If N\(_2\)-fixation events are highly episodic and related to dust input events, careful thought is needed when comparing steady state modeled N\(_2\)-fixation rates with transient snapshots of rates measured through incubation experiments.

5.6 Conclusions

We have provided new constraints on dust deposition, iron cycling, and biogeochemical dynamics in the South Pacific from measurements of water column thorium isotopes. However there are still ample opportunities remaining for future research to improve our understanding of these processes and their connections.

Our observations are consistent with the evolving framework where dissolved Th isotopes are more rapidly scavenged in the upper water column above the DCM, however we suggest that different mechanisms may be responsible for this signature in high- and low- particle flux regions. Establishing these mechanisms should a high priority, as the choice of integration depth still remains a substantial, difficult to test uncertainty in using dissolved Th isotopes to determine dust input rates. An increased number of global climate models are now simulating \(^{230}\)Th distribution (Gu and Liu 2017; Heinze et al. 2018; Hulten et al. 2018; Rempfer et al. 2017). Incorporating \(^{232}\)Th into these models, which have known dust flux fields, could facilitate sensitivity tests into how proper integration depth choice might vary regionally as a function of particle flux.

Our results suggested that models of dust flux may systematically underestimate de-
position in the central and eastern South Pacific Gyre by 1-2 orders of magnitude. Studies relying on modeled dust deposition to derive estimates of elemental input rates in these regions should consider them to be a lower bound. The residence times for dissolved iron we derived were consistent with previous observations from oligotrophic settings. Future work could constrain the input rates and residence times of other trace elements in the South Pacific. Studies of ocean trace elements are expanding to more closely connect with biological activity via transcriptomic, metabolic, and proteomic studies through programs like BIOGEOSCAPES. Thorium-based estimates of soluble micronutrient fluxes would be a valuable contribution to work of this nature, as the distributions of gene expression, metabolite production, and elemental turnover rates by microorganisms can be directly linked to geographic patterns in elemental supply.

Acknowledgements

This work was supported by U.S. National Science Foundation grant OCE-1555726 to LDEO and an NSF Graduate Research Fellowship to F.J.P. (DGE-1644869). The UltraPac Expedition (SO245) was funded by the Federal Ministry of Education and Research of Germany (Grant 03G0245A). We thank the captain and crew of the FS Sonne, as well as SO245 Chief Scientist Tim Ferdelman for ensuring safe and successful sampling. We are grateful to Bernhard Fuchs and Claudia Ehlert for assistance with pump deployment and recovery on SO245.
Chapter 6

Anomalous $^{230}$Th and $^{231}$Pa Scavenging in the deep Southeast Pacific

Abstract

Radiogenic thorium ($^{230}$Th) and protactinium ($^{231}$Pa) are commonly applied as paleoceanographic tracers of particle flux, sedimentation, and circulation, owing to their insolubility and uniform production rates by uranium decay. The burial rate of $^{230}$Th in seafloor sediments is assumed to be constant in space and time, equal to its vertically-integrated water column production rate. As such, $^{230}$Th can be used as “constant flux proxy” to reconstruct vertical sediment mass accumulation rates without bias from syndepositional redistribution, a technique deemed $^{230}$Th-normalization. However, the assumptions upon which $^{230}$Th-normalization is predicated, namely that $^{230}$Th in seawater does not experience net lateral redistribution by advection and eddy diffusion, are infrequently tested. In this study, we document anomalous scavenging of $^{230}$Th and $^{231}$Pa in the deep southeast Pacific, within the semi-enclosed Peru Basin and Bauer Basin sampled during GEOTRACES cruises GP16 and GPPr09. The confluence of weak near-bottom stratification with anomalous scavenging suggests that $^{230}$Th and $^{231}$Pa may find use as tracers of recent seafloor contact and incrop areas of water masses. We argue that the removal signatures of Th
and Pa nuclides cannot be due to local processes, and instead must reflect distal scavenging by hydrothermal particles and resuspended bottom sediments as waters flow into these basins. Direct measurements of sedimentary $^{230}\text{Th}$ burial rates at these same locations would provide a method to test amongst different mechanisms for generating the anomalous $^{230}\text{Th}$ removal and characterize the consequences for the application $^{230}\text{Th}$-normalization in the southeast Pacific.

6.1 Introduction

6.1.1 $^{230}\text{Th}$ and $^{231}\text{Pa}$ as Modern and Paleoceanographic Tracers

The long-lived radiogenic isotopes of thorium ($^{230}\text{Th}$) and protactinium ($^{231}\text{Pa}$) are used as tools for understanding particle dynamics and circulation in the modern and paleo oceans (e.g. Henderson and Anderson 2003). These two isotopes are produced at a nearly constant rate everywhere in the water column by the radioactive decay of $^{234}\text{U}$ ($^{230}\text{Th}$) and $^{235}\text{U}$ ($^{231}\text{Pa}$). Uranium is soluble, conservative, and well-mixed in the water column, so its concentration can be predicted as a function of salinity (Owens et al. 2011). Since the $^{234}\text{U}/^{238}\text{U}$ (Andersen et al. 2010) and $^{238}\text{U}/^{235}\text{U}$ (Weyer et al. 2008) ratios of seawater are also known precisely, so too are the production rates of $^{230}\text{Th}$ and $^{231}\text{Pa}$ in the open ocean.

Unlike their progenitor uranium isotopes, Th and Pa are insoluble in solution, easily hydrolyzed and rapidly scavenged by suspended and sinking particulate matter, with dissolved concentrations orders of magnitude lower than that expected from secular equilibrium with their parent uranium isotopes (Moore and Sackett 1964; Sackett 1960; Sackett
et al. 1958). The full water column residence times of $^{230}$Th and $^{231}$Pa are 20-40 years and 130-150 years, respectively (Henderson and Anderson 2003). The two elements also have variable affinities for scavenging removal by different particle types, with Th strongly removed by lithogenics and CaCO$_3$, Pa strongly removed by biogenic opal, and both elements strongly removed by Fe and Mn oxides (Chase et al. 2002; Geibert and Usbeck 2004; Hayes et al. 2015b; Pavia et al. 2018). The nearly quantitative local removal of $^{230}$Th relative to $^{234}$U in seawater led to its proposed use as a paleoceanographic tool for reconstructing vertical sediment fluxes, while correcting for lateral sediment redistribution (e.g. focusing and winnowing) at the seafloor (Bacon 1984; Suman and Bacon 1989). The short residence time of $^{230}$Th suggests that it can be negligibly redistributed by advection and eddy diffusion. Thus, the flux of $^{230}$Th reaching the sediments should be equal to its integrated production rate by U decay in the overlying water column, which is constant in space and time. The constant flux of $^{230}$Th to the seafloor implies that its concentration in sediments should be solely a function of the sedimentary mass accumulation rate (Francois et al. 2004).

The longer residence time of $^{231}$Pa allows it to be transported over greater distances by advection and eddy diffusion from regions of low particle flux (low $^{231}$Pa removal, high dissolved $^{231}$Pa concentrations) to regions of high particle flux (high $^{231}$Pa removal, low dissolved $^{231}$Pa concentrations), a process referred to as boundary scavenging (Bacon et al. 1976; Hayes et al. 2013a, 2015a. In the Pacific Ocean, coretop sedimentary $^{231}$Pa/$^{230}$Th ratios follow spatial patterns of biological productivity (e.g. particle flux), with high $^{231}$Pa/$^{230}$Th ratios near coastal margins, in the subarctic North Pacific, and in the Southern Ocean, and low $^{231}$Pa/$^{230}$Th ratios in oligotrophic gyres (Hayes et al. 2014). As a result,
downcore records of $^{231}\text{Pa}/^{230}\text{Th}$ ratios have been applied as proxies for (un)changing biological productivity in the northeast Pacific (Costa et al. 2018), Equatorial Pacific (e.g. Bradtmiller et al. 2006; Costa et al. 2016; Costa et al. 2017), and Southern Ocean (e.g. Anderson et al. 2009; Bradtmiller et al. 2009).

Application of $^{231}\text{Pa}$ and $^{230}\text{Th}$ as paleoceanography tools in some ways preceded detailed knowledge of their seawater dynamics, which has accelerated greatly since the advent of the GEOTRACES program. In particular, the assumption of negligible spatio-temporal variability of $^{230}\text{Th}$ burial rates has been directly tested only sparingly, despite recent findings of anomalous water column $^{230}\text{Th}$ behavior in near-bottom resuspended sediments (Hayes et al. 2015a) and hydrothermal plumes (Lopez et al. 2015; Pavia et al. 2019b; Pavia et al. 2018). Indeed, by normalizing to a second constant flux proxy, extraterrestrial $^3\text{He}$, Lund et al. (2019) found that $^{230}\text{Th}$ burial rates in cores from near the East Pacific Rise ridge crest exceeded their water column production rates by 50-400% during deglacial periods of increased hydrothermal activity. A better understanding of near-bottom $^{230}\text{Th}$ and $^{231}\text{Pa}$ behavior would improve their use as paleoceanographic proxies.

### 6.1.2 Typical Th and Pa Dynamics and Previous Observations in the Deep Pacific

The conventional framework for interpreting oceanic Th and Pa profiles is reversible scavenging (Bacon and Anderson 1982). For isotopes produced at a constant rate throughout the water column (like $^{230}\text{Th}$ and $^{231}\text{Pa}$), in a uniform field of particles with a constant sinking rate and neglecting lateral redistribution by advection and eddy diffusion, con-
centrations in both the dissolved and particulate phase are predicted to increase linearly with depth, reflecting reversible exchange between the dissolved pool and a slow-sinking particulate pool. For an idealized situation where an isotope has a point source at the sea surface (e.g. for $^{232}$Th), this model would predict constant depth profiles of dissolved and particulate concentration.

The assumptions inherent in the simple 1-d reversible scavenging model are generally considered to be more robust for $^{230}$Th than for $^{231}$Pa, owing to the ~order of magnitude shorter scavenging residence time of Th making it less susceptible to physical redistribution (e.g. Henderson and Anderson 2003). As such, ocean profiles of $^{230}$Th tend to be linear with depth from surface to seafloor in more ocean regions than $^{231}$Pa, which is frequently found to decrease or stay constant between the seafloor and ~1-2km from the bottom (e.g. Hayes et al. 2013a). The first locations where significant deviations from linear increases in $^{230}$Th concentrations with depth were discovered were in regions of recent deepwater formation both in the Southern Ocean (Rutgers van der Loeff and Berger 1993) and North Atlantic (Cochran et al. 1987; Moran et al. 1995, 1997) apparently reflecting the rapid transport of low-$^{230}$Th surface waters to depth.

More recently, a variety of unique deviations from linearly increasing concentration profiles have been observed for both $^{230}$Th and $^{231}$Pa. While we primarily focus on the Pacific Ocean, we will note when recent measurements from the North Atlantic show similar features. Figure 6.1 shows a summary of different dissolved $^{230}$Th and $^{231}$Pa profile shapes that have been observed in the Pacific Ocean. In the subtropical North Pacific at Station Aloha, dissolved $^{230}$Th increases linearly with depth all the way to the sea floor, reflecting the predicted reversible scavenging behavior (Figure 6.1a). In the subarctic North
Figure 6.1: Labeled schematic outlining different features observed in $^{231}$Pa and $^{230}$Th profiles from the Pacific Ocean. Panels A) and D) are from Station Aloha in the subtropical North Pacific, and are of total (e.g. unfiltered, dissolved+particulate) $^{230}$Th and $^{231}$Pa (Francois 2007). At Station Aloha, $^{230}$Th profiles are linear with depth as expected from reversible scavenging, while $^{231}$Pa begins decreasing with depth near 2500m due to processes as yet unknown. Panels B) and E) show dissolved data from the Station 41 of the INOPEX campagin in the subarctic North Pacific (Hayes et al. 2013a), documenting near-bottom removal of $^{230}$Th and $^{231}$Pa likely due to resuspended sediments. Panels C) and F) show dissolved data from the GEOTRACES GP16 section station 25 (Pavia et al. 2018) over 1000km downstream of the East Pacific Rise (EPR), with concave profiles centered at 2500m reflecting the advection of low-$^{230}$Th and $^{231}$Pa waters from hydrothermal scavenging at the EPR ridge crest.

Pacific, $^{230}$Th and $^{231}$Pa profiles cease increasing with depth $\sim$500m from the bottom, likely reflecting scavenging by resuspended particles from the sea floor in benthic nepheloid layers (Figures 6.1b and 6.1e). Just west of the EPR, concave $^{231}$Th and $^{231}$Pa profiles centered at 2500m are indicative of hydrothermal scavenging (Figures 6.1c and 6.1f).

While these myriad processes have been invoked to explain deviations from reversible...
scavenging, there are still some features that remain a mystery. At Station Aloha, the dissolved $^{231}$Pa profile bends and begins to decrease with depth below 2500m (Figure 6.1d). Since the decrease began too far from the bottom for locally resuspended sediments to be the cause, this feature was attributed to lateral transport of $^{231}$Pa to a far-field sink, hypothesized to be MnO$_2$-rich particles near hydrothermal vents (Hayes et al. 2013a). In the semi-enclosed Peru and Panama Basins, dissolved (Singh et al. 2013) and total (Okubo 2018) $^{230}$Th were shown to decrease or stay constant with depth below 1500-2000m, 2-3km above the seafloor. This anomalous $^{230}$Th behavior was attributed either to scavenging by resuspended and/or laterally advected MnO$_2$ particles.

We present water column profiles of dissolved and particulate $^{230}$Th, $^{231}$Pa, and $^{232}$Th from two zonal transects within the Peru Basin. Using these data, we suggest two new mechanisms that may be important in driving the deep scavenging anomalies present in $^{230}$Th in the SE Pacific, and in $^{231}$Pa across the Pacific subtropics. While we do not have sufficient information to differentiate the relative importance of our hypotheses, we predict the sedimentary signatures conveyed by the different processes so that future studies may make more quantitative tests. By illuminating the processes involved in setting these anomalous profiles we hope to clarify the utility of Pa and Th as tools for studying particle flux and circulation in the modern and paleo oceans.

### 6.2 Materials and Methods

We use dissolved and particulate $^{230}$Th, $^{231}$Pa, and $^{232}$Th measurements from two cruises: TN303 aboard the Thomas G. Thompson, GEOTRACES section cruise GP16 from Ecuador.
to Tahiti from October-December 2013, and SO245 aboard the Sonne, the UltraPac section also designated as a GEOTRACES process study GPpr09 between Chile and New Zealand from December 2015-February 2016 (Figure 6.2). Our focus is on data from the eastern portion of these sections, from within the semi-enclosed Peru Basin east of the East Pacific Rise (EPR). Previous work has detailed the Th and Pa distributions on the GP16 section west of the EPR (Pavia et al. 2019b; Pavia et al. 2018) and in the upper water column both from the GP16 section (Pavia et al. 2019a) and SO245 section (Chapter 5). These works have described in detail the sample collection and analysis protocols for dissolved and particulate Th and Pa isotopes from the two sections. Since the data presented here are from the same sample sets as those previously described, with identical analytical procedures, we refer the reader to the already-published works for details on Th and Pa measurements.

6.3 Results for Dissolved and Particulate $^{230}$Th, $^{231}$Pa, and $^{232}$Th

6.3.1 Dissolved Th and Pa

The GP16 data show distinct patterns in dissolved Th and Pa isotopes between stations 1-9 further to the east, and 11-17 further to the west (Figures 6.3a-6.3c). At stations 1-9, dissolved $^{230}$Th increases linearly with depth from 0-1000m with a constant slope, before increasing with a less steep slope between ~1000m-3000m, and decreasing with depth from ~3000m to the seafloor. Dissolved $^{231}$Pa follows a similar pattern to $^{230}$Th at these
stations, except that its decrease with depth begins further up in the water column, near 2500m depth. Concentrations of $^{232}\text{Th}$ are greatest closest to the coast, decreasing monotonically from station 1 to 11. The dissolved $^{231}\text{Pa}$ and $^{230}\text{Th}$ profiles at stations 11-17 share many of the same features as those at 1-9, with a couple of key differences: 1) $^{230}\text{Th}$ begins decreasing at $\sim2500$m rather than 3000m and $^{231}\text{Pa}$ begins decreasing at $\sim2000$m rather than 2500m, and 2) The magnitude of the decrease with depth is greater at stations 11-17 for both $^{230}\text{Th}$ and $^{231}\text{Pa}$. There are negligible zonal $^{232}\text{Th}$ gradients below 1000m between stations 11-17.

Dissolved $^{230}\text{Th}$ and $^{231}\text{Pa}$ profiles from SO245 (Figures 6.3d-6.3f) are distinct from those on GP16. Stations 2-6 are from within the Peru Basin at 23°S, while station 8 is from the...
western flank of the EPR outside the Peru Basin. Dissolved $^{230}$Th on SO245 increases linearly from the surface to 1500m, before decreasing to a local minimum at 2200m. At stations 2-6, $^{230}$Th increases again below this minimum until $\sim$2800m, then decreases towards the seafloor. At station 8, $^{230}$Th does not decrease sharply below 2800m, instead increasing slightly towards the bottom. Dissolved $^{231}$Pa at stations 2-8 begins decreasing below 1500m. At stations 2-6, this decrease continues all the way to the seafloor, while at station 8 $^{231}$Pa increases slightly from 2500m to the bottom. Dissolved $^{232}$Th shows negligible variation between stations 2-8, decreasing slightly from 1000m to 2000m and
6.3.2 Particulate Th and Pa

Particulate $^{230}$Th on GP16 linearly increases with depth between the surface and 250-500m above the seafloor (Figure 6.4a). Particulate $^{231}$Pa increases linearly until 2000m, then stays constant with depth until 250-500m above the seafloor (Figure 6.4b). Except for station 1, which is likely influenced by offshore transport of lithogenics from the continental slope from 1000-2500m observed in both iron and $^{228}$Ra (Sanial et al. 2018), particulate
Th is constant with depth until 250-500m above the seafloor (Figure 6.4c). Particulate concentrations of all three isotopes increase sharply in the 250-500m above the seafloor, indicative of the presence of resuspended bottom sediments in benthic nepheloid layers (Figure 6.4a-6.4c). Similar patterns exist for particulate Th and Pa isotopes on SO245 (Figures 6.4d-6.4f), the primary difference being that particulate $^{230}$Th is also generally constant between 2000m and 250-500m above the seafloor, as observed for $^{231}$Pa both on GP16 and on SO245.

6.4 Physical and Sedimentological Setting

6.4.1 Hydrography of the Basins and the Processes that Fill Them

The Peru Basin (PB) and Bauer Basin (BB) are topographically-complex semi-enclosed basins in the SE Pacific, bounded by the Nazca Ridge and Sala-y-Gomez Ridge (SGR) to the south, the EPR to the west, and the Carnegie and Cocos Ridges to the north (Figure 6.2). An extinct spreading center, the Galapagos Rise, forms a topographic high separating the Bauer Basin to the west and the Peru Basin to the east. On either side of the Galapagos Rise, topography gently slopes downward to depths of 4000m on the western side of the basin and up to 5000m on the southeastern side of the basin. From 25°S to 3°S, the EPR sill is shallower than 3000m, before deepening to 3100m between 3°S and the Equator. The Sala-y-Gomez and Nazca ridges to the south and Carnegie and Cocos Ridges to the north are both shallower than 3000m. As a result, there are significant volumes of deep water in the PB and BB below 3000m that lie beneath the sill depths of the basins.
The mechanisms by which these basins are filled below their sill depth remain unclear. Lonsdale (1976) suggested that the deepest portions of the PB are supplied by flow through the Peru-Chile Trench at ~4900m and through gaps in the Sala-y-Gomez and Nazca sills at ~3900m, while the BB is filled by eastward flow through transform faults in the EPR between 3ºS and 10ºS. However, it was also noted that waters below 3100m west of the EPR had different properties (e.g. saltier, higher $O_2$) than waters at the same depth in the BB.

Waters below ~2800m in the BB and PB also have extremely weak density stratification (Johnson and Talley 1997), implying that these basins may be filled by overflows across shallow sills in the ridges rather than through fracture zones. Johnson and Talley (1997) suggested a possible flow regime in the PB and BB where a homogenous water mass enters the basins over sills, gains buoyancy through mixing and geothermal heating to rise across the EPR sill depth, and flows into the central Pacific, feeding the westward jet observed at 15ºS.

Nutrient concentrations profiles are similar between GP16 stations in the Bauer Basin and SO245 stations 2-6 (Figure 6.5). GP16 stations 11-17 in the BB are characterized by a 2500m maximum in dissolved $O_2$, with decreasing $O_2$ and increasing dissolved $Si(OH)_4$ below 2500m (Figures 6.5a and 6.5b). The profile shapes of oxygen and silicate for SO245 stations 2-6 are similar to those from GP16 stations 11-17, but the oxygen concentrations are higher and silicate concentrations are lower, indicating a greater presence of CDW relative to PDW (Figures 6.5d and 6.5e). Profiles of oxygen and silicate at GP16 stations 1-9 are different compared to 11-17, with lower oxygen at 2500m that increases with depth, and higher silicate at 2500m that decreases with depth (Figures 6.5a and 6.5b). This sug-
Figure 6.5: Hydrographic profiles from GP16 (A-C) and SO245 (D-F). First column shows dissolved oxygen (A,D), the second column shows dissolved silicate (B,E), and the third column shows dissolved δ³He (C,F). GP16 δ³He data from Jenkins et al. (2018).

suggests different water mass structure on the east and west sides of the Galapagos Rise.

Measurements from meridional WOCE transects P18 (103°W, west of the Galapagos Rise) and P19 (88°W, east of the Galapagos Rise) support this observation. At 103°W, waters below 3000m in the BB, north of the Galapagos Rise from 16°S to 9°S, are distinct in their low-O₂ and high Si(OH)₄ compared to waters above 3000m, and compared to waters of similar depth both south of the Galapagos Rise and northwest of the EPR (Figure 6.6). At 88°W, waters north from 20°S to 8°S have increasing O₂ and decreasing Si(OH)₄.
Figure 6.6: Meridional oxygen (A) and silicate (B) sections along 103°W from the WOCE P18 section with depth below 3000m (Figure 6.7). Decreasing concentrations of oxygen and increasing concentrations of Si(OH)$_4$ from south to north either reflect mixing of CDW with an older water mass in the eastern Peru Basin, or aging of CDW as it flows northward after passing through the Nazca Ridge (Tsuchiya and Talley 1998).

Taken together, the GP16 and WOCE hydrographic data strongly suggest that the Bauer Basin has topographic restrictions in all directions that prevent inflow of waters >3000m depth. The Bauer Basin below 3000m must thus be filled by sill overflows of
Figure 6.7: Meridional oxygen (A) and silicate (B) sections along 88°W from the WOCE P19 section

waters passing over the EPR near 3°S and sinking along the topographically rough, but gently-sloped seafloor. Export of these waters from the deep Bauer Basin must occur due to buoyancy gain from geothermal heating and diapycnal mixing, allowing these waters to rise above the sill depths of their topographic restrictions and be exported.
6.4.2 Sedimentological and Geochemical Setting

Sediments in the Peru and Bauer Basins are enriched in transition metals like Fe and Mn relative to their expected concentrations from detrital (e.g. continental, lithogenic) sources (Boström et al. 1969). Hydrothermal activity on the EPR serves as a source of both dissolved and particulate Fe and Mn to seawater (Feely et al. 1996; Fitzsimmons et al. 2017; Resing et al. 2015). The origin of the metals in Peru and Bauer Basin sediments has been attributed to two primary sources: 1) transport of fine-grained hydrothermal precipitates by bottom currents flowing over the EPR sill downslope into the Bauer Basin (Dymond and Veeh 1975), and 2) authigenic (hydrogenous) precipitation of Fe and Mn minerals at the seafloor, reflected by high concentrations of Ni, Cu, and Co (Dymond and Veeh 1975).

Sediment accumulation rates in the SE Pacific basins generally track patterns of biological productivity and carbonate preservation (Heath and Dymond 1977; Weber et al. 2000). Higher biogenic particle fluxes are found close to the Equator and near the South American continent, reflecting spatial patterns of biological productivity (e.g. Behrenfeld et al. 2005). Linear sediment accumulation rates are low throughout both basins, at ~1 cm/kyr in cores above the carbonate compensation depth of 4km, and 3-10 times lower (0.1-0.3 cm/kyr) in cores below 4km (McMurtry et al. 1981).

A consequence of the metal-rich nature of the sediments, their low accumulation rate, and the low supply of organic carbon, several important modes of oxic diagenesis occur in Bauer Basin sediments. For example, a large proportion of Fe in Bauer Basin sediments is found in smectite minerals (Sayles and Bischoff 1973), reflecting the reaction
of Fe oxyhydroxides with silica either locally (Heath and Dymond 1977) or at the EPR and subsequently transported as fine grained particles into the basin (McMurtry and Yeh 1981).

6.5 Discussion: What Drives Anomalous Th and Pa Removal in the SE Pacific?

We outline possible mechanisms that could generate the observed $^{230}$Th and $^{231}$Pa depletions in the deep Peru and Bauer Basins. There is insufficient evidence to decisively select a most likely scenario. Instead, we show where there are consistencies and inconsistencies between observations and given hypotheses. We focus on what the putative sinks for the “missing” Th and Pa might be, consider the implications of each mechanism for $^{230}$Th burial rates and the application of $^{230}$Th-normalization in the SE Pacific, and suggest some ways of testing our hypotheses with future measurements.

6.5.1 Local Sediment Resuspension in Benthic Nepheloid Layers

Elevated concentrations of particulate matter resuspended from the ocean bottom have been observed extending hundreds of meters above the seafloor in zones deemed benthic nepheloid layers (Gardner et al. 2018; McCave 1986). These particles can have substantially different chemistry from the particles sinking from above. Scavenging by resuspended particles in benthic nepheloid layers has been invoked to explain abyssal $^{230}$Th and $^{231}$Pa removal due to local resuspension in the subtropical North Pacific (Okubo et al.
and from both local resuspension and lateral downslope particle transport in the North Atlantic (Hayes et al. 2015a). Metal oxides prevalent in Peru and Bauer Basin sediments have particularly high affinities for scavenging Th and Pa from seawater (Hayes et al. 2015a; Pavia et al. 2018), and could potentially play a role in driving the deep water removal of dissolved $^{230}\text{Th}$ and $^{231}\text{Pa}$.

Using optical observations of particulate matter from the GP16 section, Ohnemus et al. (2018) found benthic nepheloid layers extending several hundred meters above the seafloor east of the EPR. Optical ‘spikes’ indicative of the presence of large particles/aggregates were only found up to 150m above the bottom (Ohnemus et al. 2018). Lee et al. (2018) suggested on the basis of size-fractionated particle chemistry that distinct nepheloid layer regimes existed between stations 1-11 and stations 13-17 on GP16. Nepheloid layers at stations 1-11, nearer to the continent, were dominated by large lithogenic particles (e.g. rich in Ti and Al), while those at stations 13-17 were dominated by fine-grained metalliferous particles rich in Fe and Mn, consistent with downslope transport of hydrothermal particles during sill overflows at $\sim$3-5ºS from the EPR into the deep Bauer Basin (Dymond and Veeh 1975; Lee et al. 2018).

The depletions in dissolved $^{230}\text{Th}$ and $^{231}\text{Pa}$ extend above both the depths of observed particulate enrichments (Figure 6.8), and of the sills enclosing the basin. Furthermore, the depth of the dissolved $^{231}\text{Pa}$ depletion is shallower than that of $^{230}\text{Th}$. Scavenging by local nepheloid layers would be expected to deplete Th and Pa in the same depth range of particle resuspension unless the removal signal was physically transported differently for Pa and Th.

Previous studies in the Pacific finding anomalous $^{230}\text{Th}$ removal thousands of meters
above the seafloor suggested that near-bottom scavenging could generate depletion signatures that would be slowly mixed upwards in the water column by vertical diffusion, resulting in water column $^{230}$Th depletion extending further upwards in the water column than the particle resuspension zone (Okubo 2018; Okubo et al. 2012). For vertical diffusivities of $1$-$4 \times 10^{-4}$ m$^2$/s, Okubo et al. (2012) estimated that near-bottom removal signatures could be mixed upwards 350-750m on a timescale of 20 years (the whole ocean Th residence time). The longer residence time of $^{231}$Pa would allow for more time for vertical diffusion to mix a bottom removal signal upwards in the water column, potentially explaining the shallower onset of $^{231}$Pa removal compared to $^{230}$Th.

**6.5.2 Distal Removal by Hydrothermal Activity**

Given the complex routes waters must take to enter the Peru and Bauer Basins, including flow along rough topography, near particle-rich hydrothermal plumes, and seamount fields, it is conceivable that the depletions in dissolved $^{230}$Th and $^{231}$Pa we observe are
imparted upstream of the study areas. A similar process was hypothesized as possible explanation for decreasing $^{230}$Th and $^{231}$Pa 1-2km above the sea floor in the North Atlantic. There, Hayes et al. (2015a) suggested that deepwater flow through fracture zones could allow for extensive Th and Pa removal as waters were exposed to resuspended metal-rich particles, generating depletions that are subsequently advected into the eastern basin.

SO245 profiles of $^{230}$Th are concave with a local minimum at 2200m (Figure 6.3d), coincident with the maximum $\delta^{3}$He measured on the same section (Figure 6.5f), indicative of removal by hydrothermal scavenging. Unlike in the GP16 hydrothermal plume (Pavia et al. 2019b; Pavia et al. 2018), there is no particulate enrichment of $^{230}$Th or $^{231}$Pa on SO245 stations 2-8 (Figure 6.4). We interpret this to reflect hydrothermal scavenging at a distal location, long enough in the past that the Th- and Pa-bearing hydrothermal particles had sank out of the water column before sampling.

Previous work has found volcanic dFe anomalies at the same depths as $\delta^{3}$He peaks near the location of SO245 station 4 (Fitzsimmons et al. 2014). This was argued to be a signal transported thousands of km eastward from the EPR on the basis of circulation derived from steric height anomalies (Reid 1986, 1997). The hydrothermal $^{230}$Th and $^{231}$Pa deficits and $\delta^{3}$He peaks we observe on SO245 do not decrease monotonically east of the EPR (Figures 6.3 and 6.5), hinting at the possibility either of time-varying hydrothermal activity and scavenging, or variable eastward flow velocities. Below 2700m, waters flowing through gaps in the SGR east of 90ºW are carried westward. These waters at stations 2-6 have distinct features relative to waters of the same depth outside the Peru Basin at station 8, including higher $\delta^{3}$He, lower $O_2$, and higher silicate (Figure 6.5). The $^{230}$Th and $^{231}$Pa deficits at below 2700m at stations 2-6 are also much greater than at station 8 (Figure
6.3d and 6.3e), suggesting that scavenging is occurring either locally from resuspended sediments, or as waters flow across the SGR into the Peru Basin.

Deficits in $^{230}$Th and $^{231}$Pa on GP16 above 3000m may be due to the northward advection of this hydrothermal scavenging signature throughout the Peru and Bauer Basins. The difference in depth of the deficit between stations 1-9 and 11-17 along GP16 is consistent with the depth of the northward penetration of high-$O_2$, low silicate waters below 3500m in the Peru Basin and from 2000-3000m in the Bauer Basin evident in WOCE P19 and P18 sections, respectively (Figures 6.6 and 6.7). Additional removal at these depths may occur due to sediment resuspension as waters flow over the Galapagos Rise. However, the topographic restriction of the Galapagos Rise inhibits northward flow of waters into the Bauer Basin below 3000m, necessitating an alternative removal mechanism for Th and Pa below 3000m at stations 11-17.

### 6.5.3 Distal Removal by Resuspended Sediments

We hypothesize a new mechanism to explain $^{230}$Th and $^{231}$Pa deficits below 3000m in the Bauer Basin (GP16 stations 11-17), where neither local benthic nepheloid layers nor advection of a hydrothermal scavenging signal can feasibly result in the observed profiles. The Th and Pa deficits in the Bauer Basin coincide with weak stratification, with low vertical density gradients extending 1.5km above the seafloor (Johnson and Talley 1997). In the similarly restricted Panama Basin, just north of the Equator in the NE Pacific, waters fill the basin by sill overflows across the narrow Ecuador Trench and propagate into the interior of the basin, where they lose buoyancy from geothermal heating and abyssal mix-
ing, generating weakly stratified bottom boundary layers extending over 1000m above the seafloor (Banyte et al. 2018b).

The observation that turbulent mixing rates are greatly enhanced in regions of rough topography (Ledwell et al. 2000) has spawned an abundance of work to determine the consequences of bottom-intensified mixing on abyssal overturning and water mass transformation (e.g. Ferrari et al. 2016; Mashayek et al. 2015; McDougall and Ferrari 2017). In the Pacific, transformation of northern-flowing deep water masses (e.g. AABW) into shallower waters that return southward to the Southern Ocean (e.g. PDW) occurs by diabatic upwelling, the efficiency of which is strongly connected to the seafloor area a given density class can access (deemed an “incrop area”), where bottom-intensified turbulence can mix waters upwards (Lavergne et al. 2017). In the Panama Basin, density classes with the largest incrop areas experience the greatest transformation into lighter waters and have the thickest weakly-stratified bottom boundary layers (Banyte et al. 2018a,b).

Water masses with the greatest access to the seafloor should similarly experience strong integrated removal of $^{230}$Th and $^{231}$Pa by resuspended bottom sediments, if the seafloor contact occurred recently enough relative to the residence times of Th and Pa. These removal signatures can then be propagated vertically through the water column by turbulent upwelling and downwelling modulated by topography. If seafloor access were a common mechanism driving weak vertical stratification and Th+Pa removal, we would expect to find the strongest Th and Pa anomalies in density classes with the greatest incrop areas. The southeast Pacific has maximum incrop areas at significantly lighter neutral density classes ($\gamma_n=28.01$-$28.02$ kg/m$^3$) than the rest of the Pacific ($\gamma_n=28.05$-$28.1$ kg/m$^3$) (Lavergne et al. 2017). At stations 11-17, even though $^{230}$Th anomalies are extend
Figure 6.9: Profiles of dissolved $^{230}$Th (A), $^{231}$Pa (B), and $^{231}$Pa/$^{230}$Th activity ratio (C) plotted against neutral density from GP16 stations 11-17 in the Bauer Basin.

up to 1500m above the seafloor, they are confined to an extremely narrow neutral density range $\gamma_n=28.01-28.03 \text{ kg/m}^3$ (Figure 6.9). Thus the $^{230}$Th deficits do indeed closely coincide with the maximum incrop areas for the region, suggesting a shared mechanism related to seafloor access for the weak vertical stratification and Th+Pa removal in the Bauer Basin.

Our complete scenario linking the physical oceanography and geochemical characteristics of the deep (>3000m) Bauer Basin is as follows. Waters enter the BB across the shallowest portion of the EPR sill near 3ºS, and experience some degree of Th and Pa removal by metal-rich hydrothermal particles either in the water column or resuspended near the seafloor as they pass over the sill. The gently-sloping but rough topography between the EPR and the center of the BB allows for intense vertical mixing (Holmes et al. 2018) resulting in weak vertical stratification, and continued contact with bottom sediments allows for progressive deep Th and Pa removal.

This scenario would suggest that $^{230}$Th and $^{231}$Pa are potentially sensitive tracers of
recent seafloor contact and water mass transformation. Given its longer residence time, 
\(^{231}\)Pa would have a longer “memory” of removal by recent seafloor contact, and have its 
integrated removal signal propagated further up in the water column by vertical mixing. In the Subarctic North Pacific, \(^{231}\)Pa removal anomalies are present below \( \gamma_{n} = 28.1 \text{ kg/m}^3 \) (Hayes et al. 2013a), the density class with the maximum incrop area in the main Pacific (Lavergne et al. 2017). Future work, including upcoming meridional GEOTRACES transects through the north and south Pacific, could test this relationship by comprehensively mapping near-bottom \(^{230}\)Th and \(^{231}\)Pa depletions to neutral density surfaces and comparing them to the incrop areas of those density layers.

### 6.5.4 Burial rates of \(^{230}\)Th as means of testing amongst mechanisms, and paleoceanographic consequences

The use of sedimentary \(^{230}\)Th as a constant flux proxy (Francois et al. 2004) hinges on the assumption that its burial flux is equal to its integrated production rate by \(^{234}\)U decay in the overlying water column. Processes that cause \(^{230}\)Th to be buried in excess or in deficit of its water column production rate will bias mass accumulation rates derived from Th-normalization. Recent work has tested this assumption by measuring an independent constant flux proxy, extraterrestrial \(^3\)He, along with \(^{230}\)Th to test whether the burial rate of \(^{230}\)Th is equal to its water column production rate (Lund et al. 2019). Just west (8-30km) of the south EPR, burial fluxes of \(^{230}\)Th relative to production (F/P) reach values of 1.5-4 indicating excess \(^{230}\)Th burial, especially during deglacial pulses of hydrothermal activity (Lund et al. 2016; Lund et al. 2019).
Early work in the metalliferous sediments of the SE Pacific did not measure $^3$He, but attempted to assess $^{230}$Th burial anomalies on the basis of sedimentary $^{230}$Th inventories. Burial rates of $^{230}$Th based on these inventories can potentially be biased by lateral sediment transport (e.g. focusing or winnowing), but can be qualitatively instructive regarding relative changes in $^{230}$Th burial from location to location. Cores along the EPR had $^{230}$Th inventories greater than expected from water column production, while cores in the deep Bauer Basin had $^{230}$Th inventories 2-5 times lower than expected from water column production (Dymond and Veeh 1975; McMurtry et al. 1981).

The mechanisms we propose for explaining deepwater $^{210}$Th depletions would generate distinct patterns of $^{230}$Th burial (F/P) that can be tested by future measurements. Local scavenging by benthic nepheloid layers would be expected to bury $^{230}$Th near or above its integrated water column production rate at each station (GP16 and SO245 F/P $\geq$ 1). Distal removal by hydrothermal activity would cause burial rates to be higher than production in the near vicinity of mid-ocean ridges, including the SGR and EPR, and lower than production everywhere else in the SE Pacific where low $^{230}$Th waters are advected from the ridge (GP16 and SO245; F/P < 1). Distal removal by resuspended sediments as waters flow across the seafloor in the Bauer Basin would generate a pattern of decreasing F/P ratios from west to east in the BB. Future efforts to comprehensively map $^{230}$Th burial rates by normalization to $^3$He in the SE Pacific would be a critical step towards understanding the water column processes responsible for anomalous Th and Pa dynamics in the deep ocean.
6.6 Conclusions

We found removal signatures of $^{230}$Th and $^{231}$Pa extending thousands of meters above the seafloor in deep waters of the semi-enclosed Peru and Bauer Basins in the southeast Pacific Ocean. It is difficult to invoke local burial by conventional Th and Pa scavenging processes to explain these deficits. Instead, we suggest that distal removal by metal-rich particles both from hydrothermal activity and resuspended bottom sediments strips $^{230}$Th and $^{231}$Pa from solution as waters flow into the semi-enclosed basins, with the ensuing deficits of dissolved Th and Pa subsequently spreading throughout the basin bottom waters by advection and mixing.

We document a novel relationship between the removal of Th and Pa and weak stratification above the seafloor. The interplay between circulation and particle flux in dictating $^{230}$Th and $^{231}$Pa distributions in the Pacific may be significantly different than in the Atlantic. Seafloor access is critical for overturning and water mass transformation in the abyssal Pacific, and also should drive removal of dissolved $^{230}$Th and $^{231}$Pa by resuspended sediments. These removal signatures would be slowly eroded as they were advected downstream, via ingrowth from U decay and desorption from sinking particles – with this erosion back towards reversible scavenging profiles occurring faster for $^{230}$Th than $^{231}$Pa. Future work modeling this effect may allow for the application of $^{230}$Th and $^{231}$Pa as tracers of the timescales of seafloor access, and thus overturning, in the Pacific.

Distal removal of $^{230}$Th at topographic highs such as the East Pacific Rise, Nazca Ridge, and Sala-y-Gomez Ridge would suggest that some assumptions behind $^{230}$Th-normalization, namely the local burial of all $^{230}$Th produced in the overlying water column,
may be violated in the SE Pacific. We recommend direct measurements of $^{230}$Th burial fluxes in the region, normalized to extraterrestrial $^3$He, as a method both for determining the relative importance of different removal processes in generating water column deficits and for understanding the consequences for $^{230}$Th-normalization in the SE Pacific.

**Acknowledgements**

This work was funded by U.S. National Science Foundation grants OCE-1233688 and OCE-1555726 to LDEO and an NSF Graduate Research Fellowship to F.J.P. (DGE-1644869). The UltraPac Expedition (SO245) was funded by the Federal Ministry of Education and Research of Germany (Grant 03G0245A). We thank the captains, crews, and scientists aboard the Thomas G. Thompson and FS Sonne for their contributions to the TN303 (GP16) and SO245 (GPpr09) cruises, respectively.


Andersen, M B et al. (2010). “Precise determination of the open ocean $^{234}$U/$^{238}$U composition.” In: *Geochemistry Geophysics Geosystems* 11.12, Q12003.


Bourdon, B et al. (2000). “Evidence from 10Be and U series disequilibria on the possible contamination of mid-ocean ridge basalt glasses by sedimentary material.” In: Geochemistry Geophysics Geosystems 1.8.


Hayes, Christopher T et al. (2015c). “Thorium isotopes tracing the iron cycle at the Hawaii Ocean Time-series Station ALOHA.” In: *Geochimica et Cosmochimica Acta* 169, pp. 1–16.


Kretschmer, Sven et al. (2011). “Fractionation of $^{230}\text{Th}$, $^{231}\text{Pa}$, and $^{10}\text{Be}$ induced by particle size and composition within an opal-rich sediment of the Atlantic Southern Ocean.” In: *Geochimica et Cosmochimica Acta* 75.22, pp. 6971–6987.


Toner, Brandy M et al. “Measuring the form of iron in hydrothermal plume particles.” In: *Oceanography*.


