Biogeography in $^{231}\text{Pa}/^{230}\text{Th}$ ratios and a balanced ^{231}Pa budget for the Pacific Ocean

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Highlights:

- The subarctic North Pacific is a basin-scale sink for Pa
- Sediment Pa/Th ratios proposed to trace biogeographic provinces in the Pacific
- Sediment Pa/Th ratios insensitive to the Pacific meridional overturning circulation
- Pacific Pa budget is balanced, hydrothermal systems being a potentially significant sink

Abstract

The ratio of unsupported protactinium-231 to thorium-230 in marine sediments, $(\text{Pa/Th})_{\text{xs}}$, is potentially sensitive to several processes of oceanographic and climatological interest: deep ocean circulation, marine biological productivity (as it relates to total particle flux) and particle composition (specifically, biogenic opal and authigenic Mn). In order to attribute variations in $(\text{Pa/Th})_{\text{xs}}$ observed in sediment records to changes in specific processes through time, a better understanding of the chemical cycling of these elements in the modern ocean is necessary. To this end, a survey was undertaken of $(\text{Pa/Th})_{\text{xs}}$ in surface sediments from the subarctic Pacific (SO202-INOPEX expedition) in combination with a Pacific-wide compilation of published data. Throughout the Pacific, $(\text{Pa/Th})_{\text{xs}}$ is robustly correlated with the opal content of sediments. In the North and equatorial Pacific, simultaneous positive correlations with productivity indicators suggest that boundary scavenging and opal scavenging combine to enhance the removal of Pa in the eastern equatorial Pacific and subarctic Pacific. Deep ocean water mass ageing (>3.5 km) associated with the Pacific overturning appears to play a secondary role in determining the basin scale distribution of $(\text{Pa/Th})_{\text{xs}}$. A basin-wide extrapolation of Pa removal is performed which suggests that the Pacific Pa budget is nearly in balance. We hypothesize that through time $(\text{Pa/Th})_{\text{xs}}$ distributions in the Pacific could define the evolving boundaries of contrasting biogeographic provinces in the North Pacific, while the influence of hydrothermal scavenging of Pa potentially confounds this approach in the South Pacific.

1. Introduction

Chemical proxies of past ocean change are built upon knowledge of an association between certain elements or isotopes and a controlling ocean property or process. The ratio of the radionuclides ^{231}Pa to ^{230}Th , in excess of that supported by the *in-situ* decay of their respective parents, $(\text{Pa}/\text{Th})_{\text{xs}}$, in ocean sediments has multiple potential controls: biological productivity, total particle flux, advective overturning circulation or particle composition (Chase et al., 2002; Kretschmer et al., 2011; Kumar et al., 1993; Luo et al., 2010; Walter et al., 1999; Yu et al., 1996). To determine how variations in $(\text{Pa}/\text{Th})_{\text{xs}}$ in sediment records can be interpreted as a proxy for a process of interest, observations of $(\text{Pa}/\text{Th})_{\text{xs}}$ in oceanic environments that differ in the potentially controlling parameters are necessary.

Here we report new $(\text{Pa}/\text{Th})_{\text{xs}}$ data from the SO202-INOPEX expedition to the subarctic Pacific (Gersonde, 2012), which sampled environments of relatively high rates of biological productivity and burial of biogenic opal. To assess the influence of the Pacific overturning circulation and a larger range of oceanic particle composition and flux, we combine the INOPEX data with published surface sediment data throughout the Pacific basin. Enhanced removal of Pa due to opal scavenging is found to be the most robust influence on $(\text{Pa}/\text{Th})_{\text{xs}}$ in modern Pacific sediments. We briefly discuss how this proxy might be used in determining how the geographic distribution of particle composition, which is ultimately related to biogeographic community structure, has evolved over glacial-interglacial cycles.

2. Background and approach: potentially controlling processes

Dissolved uranium isotopes are homogeneously distributed throughout the ocean (Andersen et al., 2010; Chen et al., 1986; Weyer et al., 2008). This leads to a constant, well-known production of the daughter products ^{231}Pa (from ^{235}U) and ^{230}Th (from ^{234}U) throughout the water

column at a constant initial activity ratio of 0.093. Because of their particle-reactive, insoluble nature, Pa and Th are removed to the seafloor by scavenging onto particles on timescales of 50-200 yrs and 10-40 yrs (Henderson and Anderson, 2003), respectively (i.e., rapidly compared to their respective half-lives: 32,760 yrs for ^{231}Pa (Robert et al., 1969) and 75,690 yrs for ^{230}Th (Cheng et al., 2000)). It is their uniform source and differential timescales of removal by scavenging which make them potentially sensitive to several processes: particle flux, overturning circulation and particle composition. We elaborate on each process below and describe how we assess the associated influence on $(\text{Pa}/\text{Th})_{\text{xs}}$ distributions. Section 2.4 describes the new surface sediment data presented here and the published results used in our analysis.

2.1 Biological productivity, total particle flux and boundary scavenging

Regional variations in biological productivity are closely related, though not equivalent, to regional variations in total particle flux, as sinking particles are dominated by biogenic components, at least in most of the open ocean (Honjo et al., 2008). When lateral gradients in particle flux exist, scavenged elements are potentially removed preferentially in areas of high particle flux often associated with ocean margins, a concept termed boundary scavenging (Bacon et al., 1976; Spencer et al., 1981). More intense scavenging reduces ^{231}Pa and ^{230}Th concentrations in margin seawater to a greater degree than in the open ocean. This situation creates isopycnal gradients in concentration which should cause dispersive fluxes of both nuclides from low to high flux sites. More ^{231}Pa , relative to ^{230}Th , can be transported laterally because of its longer residence time (Bacon, 1988). This interpretation is consistent with the finding of many studies in the Pacific (Anderson et al., 1983a; Anderson et al., 1983b; Lao et al., 1992b; Yang et al., 1986) that the $(\text{Pa}/\text{Th})_{\text{xs}}$ of particulate matter and sediments from biologically productive ocean margins are generally higher than from open-ocean sites.

To assess the influence of boundary scavenging on sedimentary $(\text{Pa/Th})_{\text{xs}}$, we use satellite-derived estimates of net primary productivity (NPP) and export productivity (EP, the fraction of primary productivity which is exported below the euphotic zone). These parameters are not equivalent to particle flux, which is more relevant to scavenging, but more biological production of organic carbon at the surface (NPP) and its export to depth (EP) are both likely related to scavenging intensity (Coale and Bruland, 1987). The excellent geographic coverage of satellite records allows us to estimate these parameters for any given location. Long term annual NPP was calculated using monthly SeaWiFS-data (1997-2009, $1/6^\circ$ -resolution) and the standard VGPM algorithm (<http://www.science.oregonstate.edu/ocean.productivity>) (Behrenfeld and Falkowski, 1997). EP values were calculated according to Eq. 2 of Laws et al. (2011) as a function of the aforementioned NPP and the World Ocean Atlas 2009 sea-surface temperature (Locarnini et al., 2010) at 1° -resolution. Export productivity in the Southern Ocean is not well represented by the Laws et al. model, and therefore south of 40°S we use a modified function of for EP developed by Maiti et al. (2013).

2.2 Overturning circulation

The differential removal rates of Pa and Th by scavenging is also the basis for a potential sensitivity of sedimentary $(\text{Pa/Th})_{\text{xs}}$ to lateral advection by deep ocean circulation (Marchal et al., 2000; Yu et al., 1996). Scavenging is a reversible process, i.e. the average Th and Pa atom experiences several cycles of adsorption and desorption as they are removed to the seafloor by sinking particles (Bacon and Anderson, 1982; Nozaki et al., 1981). This causes the scavenged radionuclides to become concentrated with depth in the water column. A linear increase in concentration with depth is expected for a steady-state balance between radionuclide production and removal by scavenging in the absence of lateral circulation.

Where deep ocean ventilation occurs, surface waters with low ^{231}Pa and ^{230}Th concentrations are injected to depth. In these regions, such as the North Atlantic, observed ^{231}Pa and ^{230}Th concentrations in deep water are less than predicted by reversible scavenging (Cochran et al., 1987; Moran et al., 2002; Vogler et al., 1998). As a deep water mass ages and spreads laterally, particles sinking into it from above will experience enhanced desorption of ^{231}Pa and ^{230}Th until the higher steady-state radionuclide concentration is reached (François, 2007; Thomas et al., 2006). Because of its shorter residence time (10-40 yrs), ^{230}Th returns to a steady-state with respect to scavenging faster than ^{231}Pa (50-200 yrs). Consequently, dissolved $^{231}\text{Pa}/^{230}\text{Th}$ in deep waters are expected to increase with water mass age since ventilation.

The meridional overturning circulation of the Atlantic is believed to result in a large southward transport of ^{231}Pa relative to ^{230}Th because the ventilation timescale of that basin is on the order of the Pa residence time (<200 yrs) (Yu et al., 1996). The Pacific meridional overturning circulation (PMOC), however, occurs over longer timescales (>500 yrs) (Matsumoto, 2007) and at more zonally disperse spatial scales. The schematic overturning, a northward inflow at high southern latitudes of Lower Circumpolar Deep Water (LCDW) and subsequent upwelling in northern mid-latitudes to form a southward return flow of North Pacific Deep Water (NPDW) (Kawabe and Fujio, 2010; Macdonald et al., 2009) clearly influences the distribution of long-lived circulation tracers such as natural radiocarbon (Schlosser et al., 2001) or dissolved silicon (Talley et al., 2003), but it is unclear whether Pa is redistributed by PMOC (Hayes et al., 2013; Luo, 2013)

A complete treatment of the influence of deep circulation in the Pacific is beyond the scope of this paper and may require 3-dimensional circulation modeling with imposed particle fields and scavenging dynamics that are becoming more realistic (Dutay et al., 2009; Siddall et al., 2005). As a simplified approach, we compare sedimentary $(\text{Pa}/\text{Th})_{\text{xs}}$ with bottom water (>3.5 km) mean age

(Khatiwala et al., 2012), defined as the mean of the distribution of transit times between a location and the sea surface, estimated at 1°-resolution.

2.3 Particle composition

Marine particle types scavenge Pa and Th with differing efficiencies (Chase et al., 2002; Geibert and Usbeck, 2004; Guo et al., 2002; Kretschmer et al., 2011; Scholten et al., 2005; Yu et al., 2001). In general, it has been recognized that Pa has a higher affinity for biogenic opal (Chase, 2008; Chase et al., 2002; DeMaster, 1979; Taguchi et al., 1989) and authigenic manganese oxides (Anderson et al., 1983a; Kadko, 1980) compared with the other major sedimentary components (calcium carbonate or clay/lithogenic material), while Th is scavenged more equally among different particle types. Thus, sediment $^{231}\text{Pa}/^{230}\text{Th}$ ratios may represent the relative contribution of biogenic opal and/or manganese oxides to scavenging.

The fractionation factor (Th/Pa), F , is a measure of the intensity with which Th is scavenged relative to Pa. It is defined (Anderson et al., 1983a) as the ratio of the distribution coefficient of Th over that of Pa. Equivalently, F equals the $^{231}\text{Pa}/^{230}\text{Th}$ in seawater over $(\text{Pa}/\text{Th})_{\text{xs}}$ in sediments or particulate matter. In particulate material dominated by biogenic opal (Chase et al., 2002; Venchiarutti et al., 2011a; Venchiarutti et al., 2011b; Walter et al., 2001; Walter et al., 1997) or when authigenic Mn oxides (MnO_2 , for simplicity) are present (Anderson et al., 1983a), measured F values are close to 1. When other phases (calcium carbonate and clay) dominate, F is generally much larger, 10 to 20 (Chase et al., 2002; Luo and Ku, 1999; Moran et al., 2001). One expects, therefore, in the absence of boundary scavenging effects, areas where particles contain little opal or MnO_2 will have low particulate $^{231}\text{Pa}/^{230}\text{Th}$ due to the preference for Th during scavenging. As opal or MnO_2 content increase, relatively more Pa will be scavenged, increasing the Pa/Th ratio.

We compare $(\text{Pa/Th})_{\text{xs}}$ observations to the concentration of opal in the sediments (opal%). The preserved $(\text{Pa/Th})_{\text{xs}}$ represents equilibration with respect to scavenging onto the particles within about 1 km of the seafloor (Thomas et al., 2006), and deep particulate $^{231}\text{Pa}/^{230}\text{Th}$ is unaffected during burial (Anderson et al., 1983b; Chase et al., 2003b; Scholten et al., 2005; Taguchi et al., 1989). Unfortunately, particulate opal concentration changes during burial because of sediment diagenesis at the seafloor. Deep particulate rain of opal is nonetheless positively related to opal% in surface sediments in the equatorial Pacific and the Southern Ocean (Sayles et al., 2001). Therefore, without attempting to correct for sediment diagenesis, we use measured opal% as a qualitative indicator of opal scavenging. Paired measurements of MnO_2 and $(\text{Pa/Th})_{\text{xs}}$ are limited but we signify examples in the literature where this particle composition effect can be important. We note that sediment winnowing (the removal of fine sediments at the seafloor by deep currents) has been shown to affect surface sediment $(\text{Pa/Th})_{\text{xs}}$ (Kretschmer et al., 2011). While sediment winnowing is known to occur over large areas of the Southern Ocean (Frank et al., 1999; Geibert et al., 2005), we cannot explicitly account for this process in our evaluation without accurate age models for the cored sites, many of which are not available.

Because concurrent measurements of radionuclides and particle composition are sparse, we make an assumption that geographic variation in particle composition is largely produced by contrast in biological community structure. For instance, eutrophic conditions favor large phytoplankton such as diatoms (opal producers) while oligotrophic conditions favor small phytoplankton such as coccolithophorids (CaCO_3 producers) (Falkowski et al., 1998; Kostadinov et al., 2010). The ratio opal: CaCO_3 of sinking particles, which is positively correlated with particulate $(\text{Pa/Th})_{\text{xs}}$ globally (Chase et al., 2002), exhibits strong contrast across biogeographic boundaries in the Pacific (Honjo et al., 2008). Additionally, distributions of dissolved ^{231}Pa and

^{230}Th in the North Pacific indicate a threshold of scavenging intensity for both nuclides between the subtropical and subarctic gyres (Hayes et al., 2013). Conditions which favor certain phytoplankton and/or particle compositions arise due to inter-related environmental factors such as atmospheric circulation, light availability, nutrient availability, the position of the continents and ocean pycnoclines (Longhurst, 2006; Reygondeau et al., 2013). To extend our understanding of the Pa/Th cycle, we will spatially extrapolate within defined biogeographic provinces (Longhurst, 2006).

2.4 Materials and Methods

The new data presented here comprise a surface sediment $(\text{Pa/Th})_{\text{xs}}$ survey of the INOPEX cruise of July-August 2009 in the subarctic Pacific and selected samples for which $(\text{Pa/Th})_{\text{xs}}$ has been previously reported (Lao et al., 1992b) and new opal% data are reported here (Fig. 1). We assume modern age for INOPEX samples since the sediment-water interface was successfully collected, although independent age constraints have not been made. Sediments were analyzed by published methods for thorium, protactinium and uranium isotopes (Fleisher and Anderson, 2003) and opal (Mortlock and Froelich, 1989). U, Th and opal data from the INOPEX multicores were reported previously (Serno et al., 2014), and INOPEX seawater $^{231}\text{Pa}/^{230}\text{Th}$ data have been described (Hayes et al., 2013).

To investigate the distribution of $(\text{Pa/Th})_{\text{xs}}$ in a wider range of oceanographic conditions, we compiled available surface sediment data. In general we report $(\text{Pa/Th})_{\text{xs}}$ as corrected for detrital-supported fractions and age-decay by the original authors but in some cases this has been recalculated and some cores have only limited age constraints. For INOPEX cores, a detrital U/Th activity ratio of 0.5 was applied based on detrital sediments near Japan (Taguchi and Narita, 1995). For literature data, if not corrected for by the original authors, we assumed detrital U/Th = 0.7, the

basin-wide average (Henderson and Anderson, 2003). At locations with multiple data of Holocene age, the younger datum is used. A subgroup of sites has opal% data. We assign each site NPP, EP and bottom water age estimates only if the site is within a half-grid-node radius of the nearest gridded datum. In the case of bottom water age (mean age below 3.5 km), only sites deeper than 3.5 km are assigned an age. Bibliographic information for the database is found in the Supplemental Material (Table S1, Appendix 1). INOPEX surface sediment data will be archived at PANGAEA (pangaea.de) and the U.S. National Climate Data Center.

3. Results and discussion

3.1 INOPEX surface sediment (Pa/Th)_{xs} survey

The subarctic Pacific has long been known as a preferential sink for ²³¹Pa (Yang et al., 1986). High particulate fluxes and high opal contents of sinking particles (Taguchi et al., 1989) have been invoked to explain the enhanced removal of ²³¹Pa over ²³⁰Th in this region, through the boundary scavenging (Sec. 2.1) and particle composition (Sec. 2.3) mechanisms, respectively. The INOPEX surface sediment survey allows us to revisit these hypotheses with greater geographic resolution, higher precision (ICP-MS) measurements and more knowledge of sediment composition (opal% in particular).

Results are presented in Figure 2 of (Pa/Th)_{xs}, opal%, NPP and EP for the INOPEX and northwestern Pacific sites (Lao et al., 1992b). We do not expect oceanic Pa/Th fractionation to apply to the semi-isolated basin of the Bering Sea (sites SO202-10 through -22), and sediment from site SO202-26 (742 m water depth) was characterized by heavily-winnowed sand (Gersonde, 2012) and thus not representative of the fine fraction of settling particles assumed to carry the scavenged ²³¹Pa and ²³⁰Th. These sites are excluded in analyses of linear dependence. We report the Pearson correlation coefficient, *r*, which denotes the direction and strength of the linear

correlation between two variables. The strength of correlation is associated with the (somewhat arbitrary) categories: none, small, medium and strong for absolute r values between 0-0.09, 0.1-0.3, 0.3-0.5 and 0.5-1, respectively.

Throughout the subarctic Pacific, $(\text{Pa/Th})_{\text{xs}}$ is strongly correlated ($r = 0.67$) with opal% (Fig. 2D), consistent with opal being a major carrier phase for the removal of ^{231}Pa from the water column. Nearly all of the $(\text{Pa/Th})_{\text{xs}}$ values are above the production ratio, 0.093. Clearly, we confirm previous findings that the subarctic Pacific is a large scale sink for ^{231}Pa (Lao et al., 1992b; Yang et al., 1986). Nonetheless, there is considerable scatter in the $(\text{Pa/Th})_{\text{xs}}$ vs. opal% relationship which we cannot attribute to variations in sediment diagenesis without further information (sedimentation rate, bioturbation mixing depth, etc.) (Sayles et al., 2001). A large determinant of opal preservation at the seafloor is the total burial rate of sediments. We find, however, that in this case opal concentrations are not well correlated with total burial flux, as determined by ^{230}Th -normalization (François et al., 2004) (Fig. 2C). This indicates that opal% is driven not only by preservation but also influenced by variation in opal rain to the sediments.

In contrast, $(\text{Pa/Th})_{\text{xs}}$ has a small negative correlation with NPP in the subarctic survey (Fig. 2A, $r = -0.24$). A better positive correlation is found, however, between $(\text{Pa/Th})_{\text{xs}}$ and EP (Fig. 2B, $r = 0.61$). Thus the flux of organic carbon exported to depth (EP) may more accurately represent scavenging intensity throughout the water column than does its net production at the surface (NPP). The better correlation with EP may also be found because higher EP is often associated with diatom productivity (Buesseler, 1998) and mineral ballasting by biogenic opal enhances the downward flux of organic carbon (François et al., 2002; Honda and Watanabe, 2010).

This survey confirms that the subarctic Pacific is a basin-wide sink for ^{231}Pa . A strong association with opal concentration suggests that particle composition is largely responsible for

this chemical fractionation. Assuming steady-state, $(\text{Pa}/\text{Th})_{\text{xs}}$ ratios elevated above the production ratio require a lateral transport of ^{231}Pa to the subarctic by ocean circulation, if we further assume that ^{230}Th is laterally transported to a lesser extent than ^{231}Pa . The transport of ^{231}Pa to sites of its highest removal by opal occurs by eddy diffusion generally, but deep advection also contributes. We thus turn to the Pacific-wide survey to address the influence of PMOC while testing the other potential controlling parameters (particle flux and particle composition) under a larger range of oceanic conditions.

3.2 Pacific $(\text{Pa}/\text{Th})_{\text{xs}}$ and basin-wide statistical analysis

Confirming previous mapping exercises (Walter et al., 1999; Yang et al., 1986), our compilation of $(\text{Pa}/\text{Th})_{\text{xs}}$ in Pacific surface sediments (Fig. 3) shows three regions of enhanced ^{231}Pa removal: the subarctic Pacific, the eastern equatorial Pacific and the Pacific sector of the Southern Ocean, indicated by ratios above production (0.093). As well, the subtropical gyres show a deficit of ^{231}Pa with ratios below the production ratio. In Fig. 4, we present basin maps of the potential forcings against each of which we test for correlations with the observed $(\text{Pa}/\text{Th})_{\text{xs}}$ in Fig. 5.

We consider the sediment database statistically as a whole and in a series of zonal bands to highlight regional responses. The Southern Ocean is defined as $>40^\circ\text{S}$. An equatorial region is defined as 5°N - 10°S , and the remainder defines the North (55°N - 5°N) and South (10°S - 40°S) Pacific. We plot samples from the Bering Sea in Fig. 5 for completeness but will not interpret them for reasons mentioned (Sec. 3.1).

We exclude from the correlation analysis any sites shallower than 2 km water depth (see Fig. S1), sites with analytical uncertainty in $(\text{Pa}/\text{Th})_{\text{xs}}$ $>20\%$, and sites that are influenced by hydrothermal scavenging (Sec. 3.3). We use only deep (>2 km water depth) sites to focus on the

potential effect of deep circulation and because at shallower depths it has been suggested that the equilibration between sinking particles and the dissolved phase is not achieved (Scholten et al., 2008; Thomas et al., 2006). Hydrothermal scavenging was indicated by the presence of authigenic manganese oxide derived from hydrothermal activity, as determined by the original authors (Frank et al., 1994; Kadko, 1980; Lao et al., 1992b; Shimmield and Price, 1988; Walter et al., 1999)

Table 1 presents the correlation coefficients between $(\text{Pa/Th})_{\text{xs}}$ and NPP, EP, opal%, and bottom water age. In the whole basin, opal% is strongly correlated with and explains the most variability in $(\text{Pa/Th})_{\text{xs}}$ ($r = 0.7$). NPP and EP both display medium correlations with $(\text{Pa/Th})_{\text{xs}}$ ($r = 0.4$ - 0.5), while bottom water age shows a small positive correlation ($r = 0.12$). Opal scavenging appears to be the largest determinant of sedimentary $(\text{Pa/Th})_{\text{xs}}$ in the Pacific. Boundary scavenging mechanisms most likely contribute to the modern $(\text{Pa/Th})_{\text{xs}}$ distribution, while water mass ageing appears to have little effect.

Lippold et al. (2012) found that in the Atlantic, Pa/Th_{xs} is most sensitive to the overturning circulation in cores with low opal contents. We find that in the Pacific, Pa/Th_{xs} in cores with $<10\%$ opal (Fig. 5C, inset) still have only a small correlation ($r = 0.11$) with bottom water age. For further dissection, below we consider the indices of total particle flux (NPP and EP) and opal scavenging (opal%) for each region and then consider bottom water age in terms of the whole basin.

South of 40°S , correlation between $(\text{Pa/Th})_{\text{xs}}$ and NPP or EP is strongly negative ($r = -0.7$). This is in part due to the fact that high NPP and EP values are estimated along the subtropical frontal zone (~ 40 - 50°S) whereas the observed $(\text{Pa/Th})_{\text{xs}}$ along this latitude band is consistently low. This region of the southwest Pacific has very low sedimentation rates ($<2 \text{ mm kyr}^{-1}$) (Schmitz et al., 1986). Therefore, it is possible that the surface sediments here are not modern and the reported $(\text{Pa/Th})_{\text{xs}}$ values are too low because of uncorrected age decay. If initial

(Pa/Th)_{xs} at these high productivity (NPP > 150 gC m⁻² yr⁻¹, EP > 75 gC m⁻² yr⁻¹) sites from 40-50°S is assumed to be similar to sites with comparable productivity estimates in the North Pacific (ratios of 0.15-0.2, see Fig. 4B), an age correction of 100-120 kyr is necessary. Nonetheless, the strong positive correlation (r = 0.67) between (Pa/Th)_{xs} and opal% suggests that opal scavenging is the dominating influence here. In fact total particle flux has been found to be less important than the opal content of particles in determining (Pa/Th)_{xs} in all sectors of the Southern Ocean (Dezileau et al., 2003; Walter et al., 1999; Walter et al., 1997).

Within 10°S-40°S, little correlation with (Pa/Th)_{xs} is found between NPP and EP ($|r| < 0.17$). This region has only 1 opal% datum and is therefore not amenable to correlation analysis (Fig. 4C, Table 1). The South Pacific subtropical gyre in general lacks opal% data, even in global sediment databases (Seiter et al., 2004). Future sediment surveys in the South Pacific are required to better understand the (Pa/Th)_{xs} distribution there.

In the equatorial (5°N-10°S) Pacific, (Pa/Th)_{xs} ratios are increasingly correlated with NPP (r = 0.21), EP (r = 0.39) and opal% (r = 0.64). This situation may be analogous to that seen in the INOPEX survey (Sec. 3.1) in which opal% shows the highest linear correlation to (Pa/Th)_{xs}, and the increase in correlation from NPP to EP is related to the export efficiency of diatoms and/or the mineral ballasting effect of opal found at higher EP. Pichat et al. (2004) found that (Pa/Th)_{xs} was strongly correlated with EP in the eastern equatorial Pacific, interpreted as a clear expression of boundary scavenging. Many cores from the western equatorial Pacific, however, have higher (Pa/Th)_{xs} ratios than predicted by the trend with EP found in the east. Authors reporting these results invoked either opal or MnO₂ scavenging to explain the western equatorial results.

In the North (55°N-5°N) Pacific, (Pa/Th)_{xs} has a strong correlation with NPP, EP and opal% (r > 0.66, Table 1). This makes it difficult to separate the total particle flux and particle

composition effects in the North Pacific. In the North Pacific especially, the two mechanisms of enhanced Pa removal (total particle flux and opal scavenging) may combine.

At first glance, it might appear that water mass ageing is also hopelessly convolved in the North (and equatorial) Pacific $(\text{Pa/Th})_{\text{xs}}$ distribution (Fig. 5C), given the positive correlations between bottom water age north of 10°S (Table 1). However there are two arguments supporting the view that these correlations are spurious due to the covariance of bottom water age and opal% and to a lesser extent, particle flux (Fig. S2).

The youngest bottom water ages in the Pacific are 300-400 years. This indicates the basin is not ventilated entirely from the proximal LCDW source in Southern Ocean but more extended circulation pathways from other sources of deep water such as the North Atlantic contribute to the ventilation (Broecker et al., 1998; Khatiwala et al., 2012). After deep water formation and subsequent large-scale flow, one expects ^{231}Pa to tend toward higher concentrations most quickly within the first 200-300 years (1-2 residence times) of isolation from ventilation (Gherardi et al., 2010; Rutgers v. d. Loeff and Berger, 1993). Even if the “starting age” of ventilation (northward flow of LCDW) is taken to be ~ 400 years, the apparent positive relationship between $(\text{Pa/Th})_{\text{xs}}$ and water mass age only begins 600 years later (Fig. 5C), in the Northern Hemisphere. There is a lack of sensitivity to water mass age in the first few hundred years since perturbation by ventilation, precisely when the greatest effect is expected.

Second, south of 10°S , $(\text{Pa/Th})_{\text{xs}}$ ratios are anti-correlated ($r = -0.62$) with bottom water age, opposing the expected influence of water mass ageing. In addition to ventilation, some authors have argued that deep water $^{231}\text{Pa}/^{230}\text{Th}$ ratios are perturbed (made lower) across the Southern Ocean because of intense Pa-scavenging by opal (Negre et al., 2010; Thomas et al., 2006). Dissolved $^{231}\text{Pa}/^{230}\text{Th}$ is then expected to increase with subsequent ageing of northward flowing

water masses. While our mapping efforts (Fig. 3) clearly indicate the Southern Ocean as a large-scale sink of Pa, most likely due to opal scavenging, no measurable depletion of seawater ^{231}Pa has been found along isopycnals across the Antarctic Polar Front in the Pacific (Chase et al., 2003b). The enhanced uptake of Pa in the Southern Ocean must be balanced by Pa supply by eddy diffusion with the South Pacific gyre and/or advective contributions from NPDW or the other basins. Therefore deep water $^{231}\text{Pa}/^{230}\text{Th}$ in the Southern Ocean does not appear to be “re-set” by opal scavenging. The positive correlations with water mass age most likely results from covariance of water mass age with opal% and particle flux (Fig. S2) in the east-west sense in the equatorial Pacific and in the subtropical-subarctic sense in the North Pacific.

3.2.1 Geographic variation in seawater $^{231}\text{Pa}/^{230}\text{Th}$ and fractionation factors

When assuming a steady-state removal of Pa and Th to the sediments on the basin scale, one loses some detail in how the two elements become spatially fractionated in the water column. Water column Pa/Th distributions will be of great use in distinguishing the removal mechanisms discussed above. For instance, boundary scavenging and water mass ageing influence both the dissolved and particulate radionuclide phases whereas particle composition effects can cause a change in particle/sediment $(\text{Pa}/\text{Th})_{\text{xs}}$ without a change in the dissolved phase. Unfortunately at present the available data on water column $^{231}\text{Pa}/^{230}\text{Th}$ in the Pacific is sparse.

We have compiled the available data on bottom water (within 500 m of the seafloor) $^{231}\text{Pa}/^{230}\text{Th}$ ratio (dissolved or total, dissolved plus particulate) from the Pacific (Fig. 6A), a subset of which can be combined with underlying sediments to calculate fractionation factors (Fig. 6B). This includes the INOPEX sites for which fractionation factors are reported for the first time. Where total ^{231}Pa and ^{230}Th were used to estimate F, minor corrections for the particulate phase (18% of total for Th (Roy-Barman et al., 1996) and 4% for Pa (Nozaki et al., 1998)) were made

following Hayes et al. (2013). The range in observed seawater $^{231}\text{Pa}/^{230}\text{Th}$ activity ratio is between 0.2 and 0.6. The range in observed fractionation factors is roughly 1 to 10. Higher values are associated with the opal-poor regions of the (sub)tropical Pacific and low values are associated with the opal-rich (sub)polar regions. At least in this sparse survey, the relative range in $(\text{Pa}/\text{Th})_{\text{xs}}$ is larger than that of the dissolved ratio. Therefore, variable fractionation during scavenging must play a significant role in determining the sedimentary $(\text{Pa}/\text{Th})_{\text{xs}}$ across the Pacific.

3.3 Hydrothermal scavenging of Pa

While our correlation analysis indicates opal scavenging as the most robust influence on Pacific surface sediment $(\text{Pa}/\text{Th})_{\text{xs}}$ ratios, this analysis has excluded hydrothermal scavenging (Frank et al., 1994; Kadko, 1980; Lao et al., 1992b; Shimmield and Price, 1988; Walter et al., 1999). This effect is expressed in $(\text{Pa}/\text{Th})_{\text{xs}}$ ratios above 0.093 along or near the East Pacific Rise (EPR), markedly between 10-20°S where one expects a deficit of Pa, as observed in the rest of the South Pacific subtropical gyre, due to very low productivity (and, assumedly, opal%, Fig. 4, (Seiter et al., 2004)). One might expect similar scavenging of Pa along the length of the EPR, the Pacific-Antarctic Ridge, the Chile Rise, the Galapagos Rift, and the Juan de Fuca Ridge (all roughly indicated by the 3.5 km isobar in Fig. 3). Furthermore, particles in neutrally buoyant plumes originating from vent sites may reach up to 100 km off-axis away from the vent sites (German et al., 2002). Therefore hydrothermal scavenging is potentially a wide-spread sink for Pa throughout the deep Pacific (Hayes et al., 2013). Indeed, new observations from the Atlantic (Hayes, 2013) indicate that hydrothermal scavenging and near-bottom scavenging processes in general can have “downstream” impacts on dissolved $^{231}\text{Pa}/^{230}\text{Th}$ distributions up to 100’s of km away the site of local scavenging.

Since hydrothermal MnO₂ formation is unrelated to the overlaying biological productivity, hydrothermal Pa scavenging confounds the linkage between ²³¹Pa removal and biogeographic contrast. Studies also report enhanced scavenging of ²³¹Pa due to diagenetic MnO₂ formed in the sediments near the North American continental margin due to high organic matter inputs and redox cycling (Anderson et al., 1983a; Lao et al., 1993; Lao et al., 1992b; Shimmield et al., 1986); in this case, however, the total particle flux and particle composition removal mechanisms combine to enhance Pa scavenging as was found with the covariation of opal% and productivity indices in the North Pacific.

In addition to hydrothermal and diagenetic MnO₂, early marine geochemistry studies found that deep-sea manganese nodules have a strong scavenging affinity for Pa (Ku and Broecker, 1967; Sackett, 1966). While potentially an additional sink, subsequent studies estimated that manganese nodules are most likely relatively small contributors to the basin-wide scavenging of ²³¹Pa (Ku and Broecker, 1969; Scott, 1968).

3.4 (Pa/Th)_{xs} across biogeochemical provinces

To quantify the redistribution of ²³¹Pa throughout the Pacific, we extrapolate the observed (Pa/Th)_{xs} survey within 16 defined biogeographic provinces (Fig. 7, Table 2) (Longhurst, 2006). We make the assumption that the strongest contrasts in total particle flux, opal scavenging, and diagenetic MnO₂ (and therefore the contrasts in Pa removal) occur across these province boundaries. Each province was assigned the mean and standard deviation of the average (Pa/Th)_{xs} for all sites within the province boundaries (Table 2). We support our assumption of province-type contrast in that the variability of Pa/Th_{xs} within the provinces (average 13% RSD) is significantly lower than variability between the provinces (43% RSD). We do not extrapolate to the ARCH, TASM, and NEWZ provinces (see Fig. 3) because these are very shallow and/or not represented

by any (Pa/Th)_{xs} data. We altered the KURO province to only include area east of Japan. The APLR, ANTA, SANT, and SSTC provinces were also altered to fit within 70°W and 120°E.

The extrapolated map (Fig. 7) is a near representation of basin-wide variation in ²³¹Pa flux, or removal, to the sediments (see also Fig S3). This is because ²³¹Pa is normalized by ²³⁰Th, as a constant-flux proxy (François et al., 2004). The constant-flux approach assumes that within a given volume of water, all of the ²³⁰Th produced by uranium decay is removed to the sediments by scavenging. Thus, in order to compare the flux of ²³¹Pa between biogeochemical provinces, one needs only to take into account their relative volumes, estimated here by surface area multiplied by average water depth, estimated at 1°-resolution (Table 2). The sum of province (Pa/Th)_{xs} ratios, (Pa/Th)_{xs,i}, each weighted by its fractional contribution to the total volume, f(V)_i should equal the production ratio, 0.093, assuming steady-state for the Pacific radionuclide budget (Eq. 1). This approach assumes no advective/diffusive inputs or outputs external to the Pacific. We do not attempt to constrain inter-basin radionuclide terms, largely because of the scarcity of data from the Southern Ocean.

$$Production\ ratio\ (0.093) = \sum_i \left(\frac{Pa}{Th} \right)_{xs,i} * f(V)_i \quad Eq. 1$$

The total volume-weighted (Pa/Th)_{xs} ratio in Pacific sediments by this analysis is 0.086±0.003, slightly below the production ratio. In Table 2, we also calculate the percentage of Pa removed in each province relative to the total Pa produced in the Pacific, f(Pa removed), again assuming a basin-wide (Pa/Th) ratio of 0.093. This parameter allows us to quantify relative enhancement of Pa removal for various provinces. For instance, the combined provinces PSAW, PSAE, CCAL, KURO, CHIL, PEQD, APLR and ANTA represent 22% of the volume of the Pacific considered but they are responsible for 31% of the Pa removal. The remaining Pacific:

NPSW, NPTG, PNEC, WARM, SPSG, SSTC, and NPPF, thus represents 78% of the volume but only 62% of the Pa removal.

While we have assumed a uniform removal flux of ^{230}Th , modeling efforts (Henderson et al., 1999) and sediment trap studies (Yu et al., 2001) estimate that up to 30% of the production of ^{230}Th is redistributed into the same high productivity areas that serve as preferential sinks for ^{231}Pa . This implies that the contrast in Pa removal is greater than calculated above, but should not affect the total, basin-wide Pa removal unless Pa were being supplied dispersively from other basins. In our calculated budget, 7% of the Pacific's Pa production is unaccounted for.

Perhaps the large areas of the EPR which have yet to be mapped in terms of $(\text{Pa}/\text{Th})_{\text{xs}}$, in particular the SPSG (Fig. 3), could make up for this difference via hydrothermal scavenging of Pa. Two alternative scenarios for the apparent imbalance of Pa budget are (1) the result of undersampling the continental margins, particularly of Antarctica, where very high $(\text{Pa}/\text{Th})_{\text{xs}}$ ratios may be found or (2) the subtropical provinces underestimate the true modern $(\text{Pa}/\text{Th})_{\text{xs}}$ because of unaccounted-for age-decay. With regard to (1), the coastal provinces represent small fractional volumes, making it difficult to change the basin-wide average by this explanation. The subtropical provinces, however, represent large fractional volumes and the Pa budget is much more sensitive to the average ratios used there. Similarly, the contribution of hydrothermal scavenging, if it exists, is most likely in the South Pacific where the largest area of hydrothermal ridge systems is found (see Fig. 3). In the North Pacific therefore, we are most confident in attributing the redistribution of Pa to biogeographic contrast.

3.4 Paleo-mapping of biogeographic province contrast

Given these findings, how should variation in past Pacific $(\text{Pa}/\text{Th})_{\text{xs}}$ ratios be interpreted? In a record from a single site, independent evidence of variation in total particle flux, changes in

particle composition, or changes in deep water ventilation must be sought in order to ascribe changes in $(\text{Pa}/\text{Th})_{\text{xs}}$ to a specific process. Alternatively, mapping the spatial distribution of $(\text{Pa}/\text{Th})_{\text{xs}}$ ratios in the past provides the context to interpret the large-scale redistribution of Pa. In the modern Pacific, the influence of deep water circulation was generally found to be overridden by scavenging effects, and the deep Pacific is believed to have remained weakly ventilated since at least the last glacial maximum (Bradt et al., 2010; Jaccard and Galbraith, 2013; Jaccard et al., 2009; Keigwin, 1987; Lund et al., 2011). The mid-ocean ridge system may have remained a large-scale sink for Pa throughout the Pleistocene in the South Pacific (e.g., (Frank et al., 1994)). By contrast in the North Pacific we can attribute past redistribution of Pa as primarily due to provincial contrast in diatom productivity (opal scavenging), and to a lesser extent total particle flux and diagenetic MnO_2 scavenging (which coincide with regions of high opal scavenging in the North Pacific).

Paleo-mapping across the North Pacific subtropics (NPSW and NPTG) to the high productivity and upwelling provinces in the subarctic (KURO, PSAW, PSAE, and CCAL) would be of interest to monitor any change in the intensity of their biogeographic contrast or in the location of the province boundaries themselves. This knowledge can be further related to the physical forcings (atmospheric circulation, oceanic fronts and nutrient supply to surface waters) which define the provinces and is therefore valuable information for (paleo)climate studies (e.g., (Marinov et al., 2013; Schlosser et al., 2014)). The contrast between SANT and ANTA may also be very sensitive to regional changes in diatom productivity in the past. Unfortunately, the subtropical regions will be difficult to characterize on millennial-scale time slices as their slow sedimentation rates limit temporal resolution.

To illustrate this technique, we compiled available data for $(\text{Pa}/\text{Th})_{\text{xs}}$ from cores, including SO202-07-6 (51°16'N, 167°42'E, Serno et al., unpublished), that have dated sections of the last glacial maximum (19-24 ka) (Fig. 8) (Berelson et al., 1997; Bradtmiller et al., 2006; Bradtmiller et al., 2009; Chase et al., 2003a; Frank et al., 1994; Lao et al., 1992a; Pichat et al., 2004; Shimmield et al., 1986; Yang et al., 1995). For cores with multiple data in this age range, an average $(\text{Pa}/\text{Th})_{\text{xs}}$ was taken.

This follows Lao et al. (1992a), who invoked reduced boundary scavenging in glacial times, largely based on lower $(\text{Pa}/\text{Th})_{\text{xs}}$ ratios (with respect to modern) in cores off the coast of Oregon and Peru and slightly higher than modern $(\text{Pa}/\text{Th})_{\text{xs}}$ ratios in some interior Pacific sites. Lao et al. (1992a) suggested that higher lithogenic fluxes throughout the glacial Pacific reduced the ocean residence time of Pa enough that its lateral redistribution by dispersion was reduced. Glacial $(\text{Pa}/\text{Th})_{\text{xs}}$ ratios well above the production ratio published subsequently from large regions of the Southern Ocean (Bradtmiller et al., 2009; Chase et al., 2003a), the equatorial Pacific (Bradtmiller et al., 2006; Yang et al., 1995), the EPR (Frank et al., 1994), and one core from the subarctic (Serno et al, unpublished) suggest that Pa was redistributed laterally across the basin in a similar sense to today, although perhaps to a lesser extent. Future mapping of the poorly represented glacial subarctic Pacific could evaluate the hypothesis that the three modern regions of enhanced Pa removal persisted in the glacial ocean. This in turn would support the hypothesis that a similar biogeographic contrast in diatom productivity and particle flux existed and that the locations of the associated major ocean fronts were similar to today.

4. Conclusions

New surface sediment $(\text{Pa}/\text{Th})_{\text{xs}}$ data from the subarctic Pacific display a clear sensitivity to opal scavenging. A Pacific-wide compilation of sedimentary $(\text{Pa}/\text{Th})_{\text{xs}}$ data is also consistent

with enhanced removal of Pa due to opal scavenging. Scavenging of ^{231}Pa is additionally sensitive to the total particle flux and the abundance of particulate MnO_2 . The influence of deep water ventilation associated with the Pacific overturning circulation appears to be outweighed by opal scavenging and boundary scavenging effects. We offer the concept of biogeography to estimate a Pa removal budget for the Pacific, but note that hydrothermal scavenging may be accounted for insufficiently in this approach. The volume weighted basin-scale average $(\text{Pa}/\text{Th})_{\text{xs}}$ of the Pacific (activity ratio = 0.086 ± 0.003 , compared with the production ratio, 0.093) suggests that the Pacific Pa budget is nearly in balance. Past changes in the position of the oceanic fronts separating biogeographic provinces may be reconstructed through regional or basin-wide paleo-mapping of $(\text{Pa}/\text{Th})_{\text{xs}}$ distributions.

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Figure Captions

Figure 1. Map of coring sites for which new $(\text{Pa}/\text{Th})_{\text{xs}}$ and/or opal% data are presented here. SO202 cores (gray circles) are from the INOPEX cruise (Gersonde, 2012). Radionuclide data for *Vema* (V) and *Conrad* (RC) cores (black squares) have been previously published (Lao et al., 1992b). The scheme of bathymetric shading is displayed on the right.

Figure 2. $(\text{Pa}/\text{Th})_{\text{xs}}$ results from 31 coretops from the subarctic Pacific (see Fig. 1), excluding sites from the Bering Sea and SO202-26, versus (A) net primary productivity, (B) export productivity and (D) opal concentration. (C) shows the relationship between opal% and ^{230}Th -normalized total mass burial flux. A modern age is assumed for the samples shown here, and therefore no decay correction is necessary. Error bars are equal to or smaller than the symbol size. Reported in the insets is the Pearson linear correlation coefficient, r .

Figure 3. Map of surface sediment $(\text{Pa}/\text{Th})_{\text{xs}}$ activity ratio [A.R.] of data from this study compiled with published results (see Supplementary Material for references). Thin lines demarcate the biogeographic provinces as defined by Longhurst (2006) (see Fig. 7 and Table 2 for province names). The heavy dashed lines approximate the 3.5 km isobar which also roughly trace the mid-

ocean ridge system in the Pacific. For the INOPEX cores (Fig. 1), a modern age is assumed and thus no decay correction is made. Literature data were taken from samples of Holocene age and, in general, corrected for detrital-supported fractions and age-decay by the original authors (Sec. 2.4).

Figure 4. (A) Map of net primary productivity and (B) export productivity as estimated from satellite data (Sec. 2.1). (C) Map of opal concentration in sediments for which $(\text{Pa/Th})_{\text{xs}}$ has also been measured. (D) Map of bottom water (>3.5 km) age as estimated by Khatiwala et al. (2012)

Figure 5. Cross plots of observed $(\text{Pa/Th})_{\text{xs}}$ activity ratios in the Pacific versus (A) net primary productivity (NPP), (B) export productivity (EP), (C) bottom water (>3.5 km) age and (D) opal concentration. These sites are all deeper than 2 km water depth, have analytical uncertainties in $(\text{Pa/Th})_{\text{xs}} < 20\%$, and have not been designated in the literature to be affected by hydrothermal scavenging. Inset in C shows the $(\text{Pa/Th})_{\text{xs}}$ versus bottom water age in only cores with low opal concentrations (<10%).

Figure 6. Available (A) bottom water $^{231}\text{Pa}/^{230}\text{Th}$ activity ratios [A.R.] and (B) fractionation factors calculated between bottom water and the underlying sediment from this study and the literature (Anderson, 2002; Anderson et al., 2012; Berelson et al., 1997; Chase et al., 2003b; François, 2007; Hayes et al., 2013; Nozaki and Nakanishi, 1985; Nozaki and Yang, 1987; Yang et al., 1986)

Figure 7. Extrapolated map of $(\text{Pa/Th})_{\text{xs}}$ activity ratios [A.R.] in Pacific surface sediments generated by representing each of 16 defined biogeographic provinces (Longhurst, 2006) by the average $(\text{Pa/Th})_{\text{xs}}$ ratio observed in that province. See Table 2 for the full names of biogeographic provinces.

Figure 8. Map of $(\text{Pa/Th})_{\text{xs}}$ activity ratios [A.R.] in sediments from the last glacial maximum (19-24 ka) according to published data (see Sec. 3.4 for references). Thin lines demarcate the modern biogeographic provinces as defined by Longhurst (2006) (See Fig. 7 and Table 2 for province names). The heavy dashed lines approximate the 3.5 km isobar which also roughly trace the mid-ocean ridge system in the Pacific.

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Table 1. Correlation coefficients between Pacific surface sediment (Pa/Th)_{xs} and: Net Primary Productivity (NPP), Export Productivity (EP), sediment opal concentration (opal%), and bottom water (>3.5km) age throughout the Pacific. Bold indicates statistical significance (two-tailed p-value < 0.05)

Correlation Coefficients (r-values)

	55°N-5°N	5°N-10°S	10°S-40°S	>40°S	Full Pacific
NPP	0.66	0.21	-0.04	-0.69	0.35
EP	0.73	0.39	0.17	-0.70	0.49
opal%	0.67	0.64	—	0.67	0.70
Age	0.60	0.62	-0.15	-0.62	0.12

Number of sites in analysis

	55°N-5°N	5°N-10°S	10°S-40°S	>40°S	Full Pacific
NPP	111	42	16	49	218
EP	106	42	16	49	213
opal%	31	14	1	27	73
Age	94	25	15	42	176

Table 2. Budget of Pa removal in the Pacific. The biogeographic provinces (Longhurst 2006) are considered to have the average $(\text{Pa/Th})_{\text{xs}}$ activity ratio [A.R.] of the sites included within each province. The fractional volumes, $f(V)$, of the provinces are then used to calculate a weighted average $(\text{Pa/Th})_{\text{xs}}$ for the whole basin (box below). Further assuming a basin wide removal ratio equal to the production ratio (0.093), the volume-weighted $(\text{Pa/Th})_{\text{xs}}$ can be used to estimate the fraction of total Pa produced in the Pacific removed in each province, $f(\text{Pa removed})$.

Province	Code	No. of Sites	Avg. $(\text{Pa/Th})_{\text{xs}}$ [A.R.] $\pm$		SA [10^6 km^2]	Avg. Depth [m]	V [10^6 km^3]	$f(V)$ [%]	$f(\text{Pa removed})$ [%]
Antarctic	ANTA	28	0.141	0.047	2.8	3784	10.4	1.9	2.9
Austral Polar	APLR	2	0.174	0.002	3.0	2932	8.7	1.6	3.0
California Upwelling Coastal	CCAL	15	0.158	0.012	1.0	3853	3.7	0.7	1.1
Chile-Peru Coastal	CHIL	6	0.172	0.020	2.6	3729	9.7	1.8	3.3
Kuroshio Current	KURO	18	0.177	0.015	1.4	4713	6.7	1.2	2.3
North Pacific Polar Frontal	NPPF	19	0.085	0.006	7.2	4922	35.4	6.5	5.9
North Pacific Subtropical Gyre (West)	NPSW	8	0.087	0.017	10.5	4772	50.1	9.2	8.6
North Pacific Tropical Gyre	NPTG	13	0.045	0.006	14.7	4716	69.5	12.7	6.2
Pacific Equatorial Divergence	PEQD	24	0.098	0.008	13.7	3958	54.1	9.9	10.5
North Pacific Equatorial Counter Current	PNEC	19	0.076	0.012	9.3	3978	37.1	6.8	5.5
Pacific subarctic gyre (East)	PSAE	9	0.128	0.010	3.2	4030	12.7	2.3	3.2
Pacific subarctic gyre (West)	PSAW	10	0.177	0.011	2.9	4607	13.2	2.4	4.6
Subantarctic	SANT	12	0.089	0.009	21.5	3803	81.7	15.0	14.4
South Pacific Subtropical Gyre	SPSG	22	0.076	0.011	29.0	3827	110.9	20.3	16.5
South Subtropical Convergence	SSTC	6	0.040	0.004	5.9	3936	23.3	4.3	1.8
West Pacific Warm Pool	WARM	17	0.073	0.010	4.6	4053	18.8	3.4	2.7
Total V-weighted $(\text{Pa/Th})_{\text{xs}}$							Total		Total
0.086 0.003							546.1		92.6

Surface Sediment (Pa/Th)_{xs} [A.R.]

Extrapolated Surface Sediment (Pa/Th)_{xs} [A. R.]

Supplemental Material: Including Table S1; Figures S1, S2, and S3; and Appendix 1 (.xlsx)

Table S1. References cited for Pacific (Pa/Th)_{xs} survey and the biogeographic provinces represented by those references

Reference (in alphabetical order)	Biogeographic province(s) represented See Fig. 6 for province locations
Anderson et al., 1983	NPTG
Anderson et al., 1990	PNEC, SPSG, WARM, CHIL
Berelson et al., 1997	PEQD, PNEC
Bernat and Goldberg, 1968	NPTG
Bradtmiller et al., 2006	CHIL, PEQD, PNEC
Bradtmiller et al., 2009	ANTA, SANT
Chase et al., 2003	ANTA, SANT
Cochran and Krishnaswami, 1980	NPTG, PNEC
DeMaster, 1979	PEQD
Frank et al., 1994	PEQD
Hayes et al. (this study)	PSAE, PSAW, NPPF, KURO, Bering Sea
Huh et al., 1987	CCAL
Kadko, 1980	PNEC
Kadko, 1983	NPTG
Ku, 1966	ANTA, NPSW, SPSG
Lam et al., 2013	PSAW
Lao et al., 1992	ANTA, SANT, CHIL, NPPF, NPTG, PEQD, PSAW, Bering Sea
Mangini and Kühnel, 1987	PNEC
Mohamed et al., 1996; Mohamed and Tsunogai, 1998	KURO
Müller and Mangini, 1980	PEQD, NPTG, PNEC
Narita et al., 2003	KURO
Pichat et al., 2004	PEQD, WARM
Schmitz et al., 1986	SANT, SPSG, SSTC
Shimmield and Price, 1988	SPSG
Shimmield et al., 1986	CCAL
Taguchi and Narita, 1995	KURO, NPSW
Walter et al., 1999	APLR, ANTA, CHIL, PEQD, PNEC, SANT, WARM
Yang et al., 1986	NPSW, KURO, ARCH, NPPF, NPTG, PSAW, SANT, SPSG, WARM, PNEC, Bering Sea
Yang et al., 1995	PNEC

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Figure S2. $(\text{Pa/Th})_{\text{xs}}$ versus ^{230}Th -normalized total mass burial flux (upper left) and opal flux (upper right). Bottom left and bottom right plots show the relationship between opal concentration and export productivity (EP) against bottom water age, respectively. Note the positive covariance between opal%, EP and bottom water age in the North and equatorial Pacific. These sites are all deeper than 2 km water depth, have analytical uncertainties in $(\text{Pa/Th})_{\text{xs}} < 20\%$, and have not been designated in the literature to be affected by hydrothermal scavenging.

Figure S3. Spatial distribution of ^{230}Th -normalized total mass burial flux (A) and ^{230}Th -normalized ^{231}Pa flux (B). There is some trend of increasing Pa flux with depth (C), which is expected if Pa is removed by reversible scavenging, in particular for sites in the North Pacific and Southern Ocean (points are colored by latitude [$^{\circ}\text{N}$]). Because ^{230}Th fluxes also increase with depth (assumed in the normalization technique), $(\text{Pa}/\text{Th})_{\text{xs}}$ ratios are essentially equivalent to ^{230}Th -normalized ^{231}Pa fluxes which have been normalized by water depth. Thus the $(\text{Pa}/\text{Th})_{\text{xs}}$ ratio is a proxy for Pa removal and is not majorly biased by differencing water depth among the core sites.