Thorium isotopes tracing the iron cycle at the Hawaii Ocean Time-series Station ALOHA

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Abstract

The role of iron as a limiting micronutrient motivates an effort to understand the supply and removal of lithogenic trace metals in the ocean. The long-lived thorium isotopes (232Th and 230Th) in seawater can be used to quantify the input of lithogenic metals attributable to the partial dissolution of aerosol dust. Thus, Th can help in disentangling the Fe cycle by providing an estimate of its ultimate supply and turnover rate. Here we present time-series (1994–2014) data on thorium isotopes and iron concentrations in seawater from the Hawaii Ocean Time-series Station ALOHA. By comparing Th-based dissolved Fe fluxes with measured dissolved Fe inventories, we derive Fe residence times of 6–12 months for the surface ocean. Therefore, Fe inventories in the surface ocean are sensitive to seasonal changes in dust input. Ultrafiltration results further reveal that Th has a much lower colloidal content than Fe does, despite a common source. On this basis, we suggest Fe colloids may be predominantly organic in composition, at least at Station ALOHA. In the deep ocean (>2 km), Fe approaches a solubility limit while Th, surprisingly, is continually leached from lithogenic particles. This distinction has implications for the relevance of Fe ligand availability in the deep ocean, but also suggests Th is not a good tracer for Fe in deep waters. While uncovering divergent behavior of these elements in the water column, this study finds that dissolved Th flux is a suitable proxy for the supply of Fe from dust in the remote surface ocean.

1. INTRODUCTION

Determination of the supplies of iron to the ocean is relevant to understanding Earth’s climate and the ocean’s ecology. Ocean storage of carbon dioxide is mediated by iron supply in large areas of the ocean where Fe is a limiting resource, both today (Moore et al., 2013) and during the ice ages (Martínez-García et al., 2014). Additionally, the marine distribution of diazotrophic phytoplankton that modulate the nitrogen cycle may be determined by Fe supply rates (Ward et al., 2013). Atmospheric dust is arguably the major source of Fe to the euphotic zone (Jickells et al., 2005; Boyd et al., 2010; Conway and John, 2014; Tagliabue et al., 2014). Debate on the sources of marine Fe ensues largely because the techniques to estimate the supply rate of Fe from dust in particular, or Fe residence times in general, are only beginning to be developed.

In this study, we assess the utility of thorium isotopes in seawater to provide rate information on the Fe cycle. By pairing 232Th, sourced from dust, with radiogenic 230Th (or 234Th) that provides a timescale of thorium flux, one
can make quantitative estimates of both the total dust flux to the ocean (Hsieh et al., 2011; Deng et al., 2014) and the flux of trace metals released by dust dissolution (Hayes et al., 2013a). Our study site is the Hawaii Ocean Time-series Station ALOHA (22°45’N, 158°W) (Kar1 and Lukas, 1996; Church et al., 2013) in the subtropical North Pacific, where Asian dust is deposited in spring (Prospero et al., 2003; Boyle et al., 2005; Hyslop et al., 2013). Presenting time-series data spanning 20 years (1994–2014), we demonstrate that the behaviors of Fe and Th in seawater are consistent with a variable dust source to the surface ocean. Thorium-based fluxes indicate that the residence time of dissolved Fe in the upper 125 m of the water column is less than one year. In the sub-surface ocean (>250 m), the thorium and iron cycles begin to diverge considerably. These divergences reveal new insights into the marine geochemistry of these elements.

2. BACKGROUND

2.1. Finding the timescale: thorium removal

The rate information on trace metal cycling that we seek is obtained by exploiting the natural radioactive disequilibrium between insoluble 230Th and its soluble parent 234U in seawater. The oceanic distribution of 234U (half-life 245,620 years (Cheng et al., 2013)) is homogeneous within a few parts per thousand, as 238U concentrations vary only with salinity (Owens et al., 2011) and 234U/238U ratios vary by less than 1 per mil (Andersen et al., 2010). Therefore, the decay of 234U produces 230Th at a known rate everywhere in the ocean. Due to its particle reactivity, thorium adsorbs onto sinking particulate matter, a process called scavenging, on a timescale of years to decades, much faster than 238Th decay (half-life 75,584 years (Cheng et al., 2013)).

Thus by comparing the amount of 230Th that remains in seawater to the amount produced by U decay, one can calculate a removal timescale (Eq. (1), Fig. 1), or residence time (τ), of thorium in seawater. Eq. (1) is written with radionuclide concentrations in terms of activity (decays per unit time per unit seawater). The denominator contains a 230Th term to account for 230Th-decay, which, as mentioned above, can be neglected on the timescale of water column processes (for instance, seawater 234U activity is 46.6 mBq/kg at salinity 35, while typical 230Th activities are 1–10 μBq/kg). This approach is analogous to that used with a more commonly used flux tracer, the shorter-lived 234Th (half-life 24.1 days). By the same principles, using its production rate from parent isotope 238U, 234Th inventories can also be used to determine the scavenging rate of Th in seawater (Coale and Bruland, 1985; Buesseler et al., 1992), except that 234Th-decay is much more significant in the water column balance (238U activities being ~40 mBq/kg compared to euphotic zone 234Th activities of 30–40 mBq/kg).

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\tau_{Th}(z) = \frac{\int_0^z 230Th \, dz}{\int_0^z (234U - 230Th) \, dz + \lambda_{230}dz}
\] (1)

To meet the requirements of a steady-state assumption between source and removal terms, we calculate thorium residence times in an integrated sense, from the surface to a particular depth. Thus as one integrates deeper into the water column, the 230Th inventories reflect longer timescales of removal. Residence times calculated in this way also neglect dispersal fluxes by ocean circulation. Lateral gradients in oceanic 230Th concentrations are generally small (Hayes et al., 2015a), while large vertical gradients may make vertical fluxes significant, for instance due to upwelling (Luo et al., 1995).

2.2. Finding the source: lithogenic metal fluxes

The dominant isotope of seawater thorium is primordial and long-lived (half-life 1.41 × 10^9 years) 232Th. It is added to the ocean only through the partial dissolution of continental material, which in the context of Station ALOHA we consider to be primarily aerosol dust. Once in the water column, 232Th is assumed to undergo scavenging removal (Fig. 1) at the same rate, i.e. with the same residence time, as 230Th (or 234Th), as scavenging tendencies are characteristic of all isotopes of an element. Assuming a steady state for Th concentrations, with knowledge of the Th residence

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Fig. 1. Tracing the Fe cycle with the behavior of the long-lived thorium isotopes. Thorium-230 has a well-known source from the radioactive decay of its parent 234U. This allows a quantitative estimate of Th removal due to scavenging on to particles. This removal rate can be used to estimate the steady-state source of 232Th from the partial dissolution of aerosol dust, assuming dust dissolution and scavenging dominate the Th cycle which may be most relevant in the remote surface ocean. While Fe has many more terms in its biogeochemical cycling, its ultimate source from dust dissolution can be predicted using known 232Th fluxes and the relative solubility of Fe and Th. Assuming Fe is derived only from dust, one can then estimate a maximum Fe residence time or minimum turnover rate.
time derived from $^{230}$Th, one can calculate the flux of dust-derived $^{232}$Th necessary to support the observed $^{232}$Th inventory (Eq. (2)). As in calculating thorium residence times, the derived dissolved $^{232}$Th flux is reflective of the integrated depth zone, rather than at a particular depth. More details on $^{232}$Th flux calculations are reported by Hayes et al. (2013a).

$$^{232}\text{Th flux}(z) = \frac{\int_0^z ^{232}\text{Th} \, dz}{T_{232\text{Th}}(z)} \quad (2)$$

In comparison to the relative simplicity of the supply and removal terms in the thorium cycle, seawater iron cycling has many more terms to consider. These include biological uptake, remineralization, redox chemistry, anthropogenic or hydrothermal sources, in addition to supply by dust and removal by scavenging (Fig. 1). Scavenging of Fe also occurs but at a different rate than that of Th. The utility of this element pair is their common source from dust. This is, of course, an idealization of the “simple” thorium cycle. Th will be involved to some extent with (perhaps inadvertent) uptake into and remineralization from organic matter (Hirose and Tanoue, 1994; Barbeau et al., 2001). We have also observed a strong hydrothermal sink for Th in the Atlantic (Hayes et al., 2015a) in addition to an abyssal source of Th from sediments in the North Pacific (Hayes et al., 2013a). Nonetheless, particularly in the remote surface ocean well above the seafloor, dust dissolution and scavenging appear to be the dominant terms for Th cycling. Thus, in this manuscript we propose using dissolved $^{232}$Th flux as a proxy for the Fe released during dust dissolution. This can be done with knowledge of the Fe/Th ratio in the dust and the relative fractional solubility of the two elements ($S_{Fe/Th}$ Eq. (3)):

$$\text{Dust-dissolved Fe flux} = \text{dissolved}^{232}\text{Th flux} \times (\text{Fe/Th})_{\text{dust}} \times S_{Fe/Th} \quad (3)$$

By weight, the Asian desert dust that undergoes long-range transport over the North Pacific contains $^{232}$Th at $14.3 \pm 0.8$ ppm, based on fine grained (<8 μm) source materials (McGee, 2009; Serno et al., 2014), and Fe at $3.8 \pm 0.4\%$, based on a literature compilation by Mahowald et al. (2005). Therefore, we assume the Fe/Th ratio in dust at Station ALOHA of $2660 \pm 320$ g/g or $11,040 \pm 1450$ mol/mol. These ratios are close to the average for the upper continental crust of Fe/Th = $3271 \pm 320$ g/g = $13,553$ mol/mol (Taylor and McLennan, 1995).

The relative fractional solubility of Fe and Th in dust is currently unconstrained. Hayes et al. (2013a) assumed $S_{Fe/Th} = 1$ as a starting point, based solely on the similarly insoluble nature of these two elements in seawater. While much more work is needed to constrain this parameter, here we continue to assume $S_{Fe/Th} = 1$, and our observations of the time-series variability in the seawater Fe/$^{232}$Th ratio (Section 4.4) support this assumption.

2.3. Iron residence times

We cannot rule out significant marine Fe sources by anthropogenic (e.g., derived from fossil fuel combustion) aerosols, continental margin sediments, or deep-sea hydrothermal vents. We can, however, pursue the notion that if dust were the only Fe source to the water column, the comparison between measured dissolved Fe inventories to the source (dust-dissolved Fe flux) would produce a measure of the turnover rate or residence time of dissolved Fe in seawater (Eq. (4)). This residence time again represents the residence time within the integrated water column. Additional sources of Fe, such as combustion aerosols or hydrothermal fluids, would cause the dust-based Fe residence time to be an overestimate. Relevant to iron cycling, this residence time provides a rough timescale over which one can expect Fe concentration to vary as a result of variation in sources, such as springtime Asian dust events (Boyle et al., 2005).

Dissolved Fe residence time

$$= \text{Fe inventory} \div \text{dust-dissolved Fe flux} \quad (4)$$

3. MATERIALS AND METHODS


Samples were collected on several cruises on the R/V Kilo Moana, led by the Center for Microbial Oceanography: Research and Education (C-MORE), to Station ALOHA in July–September 2012 (HOE-DYLAN), May–June 2013 (HOE-PhoR-I), September 2013 (HOE-PhoR-II) and March 2014 (HOE-BOE-I). Depth profiles for $^{230}$Th/$^{232}$Th analysis were collected from the ship’s Niskin bottle rosette, filtered with a 0.45 μm Acropak cartridge filter, and acidified to pH 1.8 with Savillex-distilled 6 M HCl.

Filtered surface seawater (0.4 μm) was collected for $^{232}$Th (which requires smaller volumes than for $^{230}$Th), as well as for dissolved Fe, using the trace-metal clean MITESS sampler (Bell et al., 2002) at near daily time intervals on the 2012–2013 C-MORE cruises. MITESS collection methods, including “Vane” sampling for Fe depth profiles, on the HOE campaigns are discussed fully by Fitzsimmons et al. (in press). Within 3 h of collection, the seawater was filtered using 0.4 μm polycarbonate track etch filters (PCTE, Whatman). Particulate samples were immediately frozen, and dissolved filtrates were acidified to pH 2 with trace metal clean HCl. The filters used for filtering MITESS water were analyzed for particulate Fe and $^{232}$Th (representing on average 0.7 liters of seawater).

On HOE-PhoR-II, cross flow filtration was performed to assess colloidal $^{232}$Th/$^{230}$Th using protocols developed to study colloidal Fe (Fitzsimmons and Boyle, 2014a). Seawater was pre-filtered at 0.45 μm and, within 1–2 h, pumped over a Millipore Pellicon XL filter made of regenerated cellulose with a nominal molecular weight cutoff of 10 kDa, roughly equivalent to an effective pore size of 10 nm. Both permeate and retentate fractions were analyzed to determine any loss of Th by adsorption, which turned out to be minimal (88–100% dissolved Th recovery).

3.2. Hawaii Ocean Time-series (HOT) seawater

Seawater samples, typically 0.5 L size, have been collected during the HOT program for trace metal analysis at MIT periodically since 1997. Most of these samples were
collected as unfiltered water using the MITESS sampler (Bell et al., 2002) and subsequently preserved by acidification to pH 2 with HCl. We report data from samples collected via ship-based MITESS collections as well as MITESS units deployed on a mooring (1997–2000, 2004–2005). In ship-board sampling, a sample bottle filled with high-purity dilute (~0.001 M) HCl is lowered over the side on a clean-wire and opened at depth, allowing ~15–20 min for the bottle to be completely flushed with the denser seawater, before bottle closure and sample retrieval. The moored sampling worked similarly except that bottles were filled with stronger acid (1 M HCl) prior to sampling. The moored sampling potentially posed a metal contamination risk due to the effective stronger leaching of the HDPE bottles, increasing the chance for leached Th, for example, to remain in the sample bottle at the time of collection. We report the moored sampler data with a unique symbol in our figures and interpret them with caution. Further sampling details are given by Boyle et al. (2005).

We also make use of literature seawater 232Th/230Th data, collected at Station ALOHA in September 1994 (HOT-57), reported by Roy-Barman et al. (1996).

### 3.3. Thorium and iron analyses

Dissolved 230Th concentrations at Station ALOHA are as low as 10–18 moles per kilogram seawater (10–18 mol 230Th = 0.1746 μBq). Therefore, for measurement by inductively-coupled plasma mass spectrometry (ICP-MS), 4–5 L water samples are required. Thorium concentrations were determined by isotope dilution by spiking with 232Th (not present in natural seawater). Sample preparation (pre-concentration, acid digestion, and chromatographic purification) was performed using published methods (Anderson et al., 2012; Auro et al., 2012). A portion of the 230Th samples were prepared and analyzed at the Lamont-Doherty Earth Observatory (L-DEO), using an Element XR single-collector ICP-MS. The remaining 230Th samples were prepared at the Massachusetts Institute of Technology (MIT) and analyzed using a Neptune Plus multi-collector ICP-MS at Brown University. Th-232 was also analyzed in samples prepared for 230Th.

Analysis of 232Th, at 10–15 mol (i.e. femtomoles) per kg seawater, required smaller samples (200–800 mL) and was measured on archive HOT and HOE samples for which sample volume did not allow 230Th determination. While not as prone to contamination as some other trace elements, clean lab techniques were required to produce blanks that were consistent and low enough to allow detection of the relatively small sample size of ~20–40 femtomoles 232Th. Therefore, modifications of the cited procedures for Th analysis (Anderson et al., 2012; Auro et al., 2012) were made. Instead of co-precipitation with added Fe, pre-concentration of 232Th was achieved using magnesium hydroxide co-precipitation, such as that described for Pb by Reuer et al. (2003). Thorium was purified using a smaller amount (100 μL rather than 1 mL) of anion-exchange resin (AG1-X8) on columns fashioned from Teflon shrink-tubing. Samples were loaded onto AG1-X8 resin in 8 M HNO₃ and Th was eluted with 6 M HCl (instead of 12 M HCl, to reduce acid blank), following Edwards et al. (1987). Blank determinations were made on 125 mL aliquots of acidified seawater samples whose 232Th content had been determined during previous 230Th analysis. The mean procedural blank (n = 6) was 3.5 ± 1.6 fmol 232Th, resulting in a detection limit of 4.8 fmol 232Th. Samples for seawater 232Th were prepared and analyzed at MIT, using a Micromass IsoProbe multi-collector ICP-MS with detection by a Daly-style ion counter.

In this study, we refer to measured trace metal concentrations as dissolved (filtered at 0.4 or 0.45 μm), particulate (>0.4 μm), or total (acidified unfiltered water). The “total” concentrations in this sense are sometimes referred to as “total dissolved”, allowing for the possibility that some forms of Th are not mobilized into solution by acidification to pH 2 or collected with co-precipitation. Since our goal in interpreting seawater 230Th concentrations is to determine scavenging rates based on uranium decay, we made small (0–10%) corrections for the dissolved 230Th released from dust (or lithogenic material in general). This correction is based on measured dissolved 232Th and a lithogenic 230Th/232Th mole ratio of 4 × 10–6 (Roy-Barman et al., 2009). The corrected dissolved 230Th values are denoted as “Xs”.

Particulate 232Th and particulate Fe, were analyzed at Florida State University by total digestion of the filter samples and subsequent analysis by ICP-MS, using slightly modified versions of published protocols (Upadhyay et al., 2009; Ho et al., 2011; Morton et al., 2013). In brief, samples were microwaved (CEM MARS Xpress) for 40 min at 180 °C with HNO₃ and H₂O₂ (to digest the organic and less refractory biogenic and authigenic components) and HF (to digest the more refractory lithogenic components). The detection limit (based on 3 standard deviations of the digested acid blanks) for particulate 230Th was 8 fmol/L (n = 19) and the particulate Fe detection limit was 0.2 nmol/L (n = 21). Dissolved Fe was measured by isotope dilution after pre-concentration onto nitritotriacetate resin on the Micromass IsoProbe ICP-MS at MIT (Lee et al., 2011). Further details on Fe analyses are discussed by Fitzsimmons et al. (in press).

Data presented in this study can be accessed in the Supplemental Material online.

### 4. RESULTS AND DISCUSSION

#### 4.1. 230Th–232Th depth profiles to 1.5 km

We focus first on the 2012–2013 thorium isotope depth profiles in the upper 1.5 km of the water column for a sense of the type of data used to calculate thorium fluxes (Fig. 2). High resolution depth profiles were analyzed in late July 2012, early June 2013 and late September 2013. The mixed layer depths during these sampling casts (based on 0.125 kg/m³ density change) were 54, 33 and 53 m, respectively, and below 100 m these profiles displayed little distinguishing hydrography (Figs. 2C–E).

For dissolved 232Th (Fig. 2A), there were increased concentrations near the surface, minimum concentrations at
the depth of maximum chlorophyll concentration (the DCM, \(\sim 120–140\) m), and a relatively constant local concentration maximum at 500–600 m depth. At intermediate depths (900–1200 m), each profile exhibited smooth variations in concentration, but concentrations at the different sampling dates varied by up to 30%.

The surface \(^{232}\text{Th}\) maxima are consistent with aerosol dust as the major source of \(^{232}\text{Th}\) to Station ALOHA, as recognized by Roy-Barman et al. (1996). An interesting feature of these high-depth resolution measurements is that the surface \((5\text{ m})\) \(^{232}\text{Th}\) concentration was lower than that in the core of the mixed layer \((25\text{ m depth})\) at these three sampling times. This is perhaps related to small-scale scavenging and export dynamics, or particle cycling in general.

The coincidence of the subsurface chlorophyll maximum and the minimum in \(^{233}\text{Th}\) is apparently a universal feature for lithogenic trace elements such as Al, Ti and Fe (Dammshauser et al., 2013; Fitzsimmons and Boyle, 2014b; Ohnemus and Lam, 2015). This was also true for dissolved and particulate Fe at Station ALOHA during this study (Fig. 7). Increased particle aggregation efficiency, such as through the formation of fecal pellets, may more efficiently scavenge dissolved \(^{232}\text{Th}\) from this depth.

Scavenged \(^{232}\text{Th}\) may be partially released through remineralization of particles from the near-surface upon sinking to mesopelagic depths \((300–500\text{ m})\). This remineralization may be responsible for some of the subsurface \(^{232}\text{Th}\) maxima at 400–600 m depth. In support of this view, this depth range coincides with a rapid increase in phosphate concentration and apparent oxygen utilization, as inferred from HOT climatology (http://hahana.soest.hawaii.edu/hot/trends/trends.html). On the other hand, the attenuation of particulate organic carbon at Station ALOHA is most intense at shallower depths, between 100 and 200 m (Bishop and Wood, 2008).

The dominant basalts of the Hawaiian Islands (tholeiitic) are low in Th content, 0.8 ± 0.4 ppm, according to available data in PetDB (www.earthchem.org/petdb) (Lehnert et al., 2000). Nonetheless, with our seawater observations, we cannot fully rule out lateral input of Th from the Hawaiian Islands. For instance, dissolved Mn concentrations reach a maximum near 800 m depth at Station ALOHA (Boyle et al., 2005) that may reflect a coastal source of metals.

The variability in \(^{232}\text{Th}\) concentration at intermediate depths \((900–1400\text{ m})\) could be due to the effect of hydrothermal activity at the nearby Loihi seamount. The
iron and other hydrothermal plumes strongly scavenge Th, and depleted deep-sea Th concentrations have been observed up to 1400 km away from a vent site in the Atlantic (Hayes et al., 2015a). While intermediate water 232-Th variability suggests the influence of hydrothermal scavenging here, the effect is apparently too weak to perturb the near-linear 230-Th profiles (Fig. 2). Time-variability in the influence of the Løilhol hydrothermal system on trace metals at ALOHA is discussed more fully by Fitzsimmons et al. (in press).

The 230-Th profiles also displayed interesting temporal variations. The theory of reversible scavenging contends that a steady-state is achieved between thorium adsorption and desorption on uniform particles that settle at a constant rate (Bacon and Anderson, 1982). Under these assumptions, one expects 230-Th concentrations to increase linearly with depth with a boundary condition of zero concentration at the surface. While the observed depth profiles are essentially linear (Fig. 2B), it appears that mixing at the surface homogenizes 230-Th concentrations to some depth. Interestingly, the layer of relatively homogeneous 230-Th extends deeper than the density-defined mixed layer (30–50 m), down to the deep chlorophyll maximum (Fig. 2; see also report by Barone et al. (2015)). This phenomenon is worthy of future time-series study. Potentially a remnant of deep winter mixed layers (>100 m), the homogeneous surface 230-Th layer could also represent some combination of vertical mixing and enhanced scavenging related to export of organic matter from the euphotic zone.

Another significant observation is that while the surface 230-Th concentrations from June and September 2013 were nearly identical (1.2 μBq/kg), the surface 230-Th concentrations from July 2012 were about a factor of 2 lower (0.6 μBq/kg). This implies a relatively rapid change in scavenging and/or export production. Future time-series studies are warranted to further assess the short-term (daily-monthly) variability in euphotic zone 230-Th concentrations and how closely these changes can be correlated with organic matter export. In the next section, we assess what changes in the removal timescale are implied by these results.

4.2. Surface thorium residence times

Residence times of dissolved 230-Th as described in Section 2.1 using the 2012–2014 results are presented in Fig. 3. In this assessment, we integrate production due to 234-U decay (based on salinity) and the measured 230-Th inventory to 150 m depth. This allows comparison to surface 230-Th inventories, which could influence the derived residence time. Assuming a vertical eddy diffusion coefficient (Kv) of 10⁻² m²/s (Charette et al., 2013), using a linear regression of the 230-Th depth profiles (from 150 to 300 m), we can calculate the 230-Th added to the upper 150 m by vertical mixing as K_v × d[Th]/dz. The results indicate that this vertical mixing term is 3–5% of the integrated production due to 234-U decay in the upper 150 m. Therefore we can assume that vertical eddy diffusion does not significantly affect the 230-Th residence time estimates at Station ALOHA.

Nearly all of the thorium residence time estimates fall in the range of 1–3 years with no evident seasonal cycle (Fig. 3). In the HOT climatology, organic carbon export at 150 m is highest in May–August. While export seasonality is relatively weak in this oligotrophic, subtropical location (Church et al., 2013), long-term monitoring has revealed episodic export events related to diatom blooms and symbiotic cyanobacteria, typically in late July and early August (Karl et al., 2012).

The concept of “residence time” used here is based on a steady-state assumption for sources and sinks. Therefore with a residence time of ~2 years, one would not expect significant variation in the removal timescale over a period of months. However, the range in observed Th residence times for Station ALOHA indicates that this steady-state assumption is not quite correct. More precisely, the steady-state for scavenging removal of Th appears to hold within a factor of 2–3. The range in removal timescales based on 230-Th is similar to that based on 238-Th. Thus, it seems the rate of thorium scavenging can change dynamically at Station ALOHA possibly related to export pulses, but the data are consistent with a long-term average thorium residence time of 2 ± 1 years in the upper 150 m.

4.3. Surface 232-Th concentrations

With relatively good control on the removal timescale of thorium, we turn to observed variability in surface 232-Th concentrations. Barring significant fluxes due to lateral circulation, this variability represents the balance between removal by scavenging and input by dust. Smaller volume requirements for analysis (<1 L) allowed us to investigate 232-Th from daily, monthly and decadal timescales.

Collected during a series of cruises in summer 2012 (HOE-DYLAN), daily-scale samples of 250 mL were analyzed for dissolved and particulate 232-Th. Sample size required combining the samples from 2 to 4 days for dissolved 232-Th, contributing to some temporal smoothing. Dissolved concentrations ranged from 45 to 90 fmol/kg (Fig. 4C). Particulate 232-Th, although measured at a higher, daily resolution, had a higher range of variability, from 10 to 290 fmol/kg. Of the total seawater 232-Th (dissolved + particulate) during HOE-DYLAN, on average 42% was in the particulate phase (range 26–66%). This
Fig. 3. Thorium residence times, or turnover rates, calculated for the upper 150 m at Station ALOHA on a monthly axis combining data from 1999 to 2014. These times are calculated by comparing integrated Th inventories to integrated production by uranium decay. The $^{234}\text{Th}$-based results are reported by Buesseler et al. (2009) and Benitez-Nelson et al. (2001). Note the $^{230}\text{Th}$-based results from March 2014 are not based on profiles but on single samples from 25 m, assuming uniform concentrations in the upper 150 as seen in the 2012–2013 profiles (Fig. 2).

Fig. 4. Station ALOHA time-series data from the surface ocean (0–10 m depth) on dissolved (filtered at 0.45 or 0.4 μm), total (unfiltered) and particulate (digested 0.4 μm filter) $^{232}\text{Th}$ in full time-series (1994–2014) (A), monthly climatology (1991–2014) (B) and during a daily resolution period in July-Sept. 2012 (C). Note change in scale of y-axes at 160 fmol/kg. Results from 1994 were reported by Roy-Barman et al. (1996). Open circles represent samples collected using a mooring rather than ship-based sampling (Section 4.1). Relative uncertainty in dissolved, total and particulate $^{232}\text{Th}$ concentrations was 1–10%.
fraction particulate is higher than that for $^{230}\text{Th}$ (~15%, Roy-Barman et al., 1996) since particulate $^{232}\text{Th}$ represents both adsorbed Th and structural Th in mineral dust.

The decadal time-series observations (1994–2014) of total $^{232}\text{Th}$ (Fig. 4A) exhibit a range in concentration (~50–300 fmol/kg) that is consistent with the higher frequency observations of particulate Th in 2012–2013. Since most of the data fall within the range of 50–150 fmol/kg, we are not fully confident in the five observations of elevated concentrations (150–300 fmol/kg) observed in 1994, 1998, and 1999 samples. In particular, the 1998 and 1999 samples were collected using the moored MITESS units, as discussed in Section 3.2. Moorung-collected water at times had higher Th concentrations than contemporaneous ship-based sampling (Fig. 4) and thus the possibility of contamination during sampling, sample storage, or sample analysis cannot be fully discounted. In fact, the variable 1994 results from Roy-Barman et al. (1996) came from multiple samples collected on the same Niskin bottle cast. Spatial variability, related to mesoscale eddies, is another potential source of rapid changes in surface $^{232}\text{Th}$ concentration. Conservatively excluding the elevated observations >150 fmol/kg, no significant temporal trend can be derived.

When all observations are placed on a monthly axis (Fig. 4B), there is little indication of elevated surface $^{232}\text{Th}$ concentrations during the spring (Mar-Jun) season of Asian dust transport over the North Pacific. It appears that dissolved $^{232}\text{Th}$ may be relatively constant throughout the year, consistent with the Th residence times of ~2 years derived in Section 4.2. Unfortunately, few observations of dissolved $^{232}\text{Th}$ have been yet made during the spring season when dust input can increase by 2 orders of magnitude (Hyslop et al., 2013). Of course, these data are sparse, but they do provide a baseline of variability against which future trace metal observations can be measured.

4.4. Fe/Th ratio behavior in surface water and in colloidal content

Before applying the $^{232}\text{Th}$ flux technique, comparison of the time-series behavior of Fe (Fitzsimmons et al., in press) and $^{232}\text{Th}$ is informative in terms of relative solubility and relative removal rates (Fig. 5). This is possible because both elements have been analyzed on the same samples from HOE-DYLAN, HOE-PhoR and many of the HOT archive samples.

In the context of daily, monthly and decadal variability, it appears that the ratio of total and particulate Fe/$^{232}\text{Th}$ tends to be at or above the dust-ratio of 11,040 mol/mol, while dissolved Fe/$^{232}\text{Th}$ is at or below the dust-ratio (Fig. 5A and B). These observations are consistent with input at the dust Fe/$^{232}\text{Th}$ ratio and a strong sink from biological uptake for Fe. Thus, the dissolved phase is left depleted in Fe relative to $^{232}\text{Th}$, while the particulate phase becomes enriched in biogenic Fe. The total Fe/Th ratio often exceeds the dust ratio as well, possibly because biogenic particulate Fe may be efficiently recycled and thus may reside in the surface longer than particulate Th. Interestingly, the samples from moored MITESS units (open symbols in Fig. 5) had Fe/Th ratios quite close to the near-crustal ratio of Asian dust. This fact does not necessarily exclude the possibility for Th contamination in these samples but does suggest any potential metal contamination was of near-crustal composition.

The partitioning between dissolved and total/particulate Fe/$^{232}\text{Th}$ centers on the dust ratio (Fig. 5C). We interpret this to mean that the relative fractional solubility of Fe and $^{232}\text{Th}$ (S$_{Fe/Th}$) is close to 1. An alternate interpretation would be that $^{232}\text{Th}$ is more efficiently leached from dust, leaving the particulate phase enriched in Fe/$^{232}\text{Th}$ and the dissolved phase depleted in Fe/$^{232}\text{Th}$. However, given the known ability for phytoplankton to efficiently utilize Fe from dust sources (e.g., (Rubin et al., 2011)), the assumption of S$_{Fe/Th} = 1$ during dissolution followed by rapid biological uptake of Fe seems more likely. It is difficult to assign a quantitative uncertainty to the relative solubility with the existing data. The measured seawater Fe/$^{232}\text{Th}$ ratios (n = 30) are on average within 54 ± 51% (1 sigma) of the Asian dust ratio. Therefore, the relative solubility is likely close to 1 with less than 50% uncertainty, but 50% could be used as a conservative uncertainty estimate (S$_{Fe/Th} = 1 ± 0.5$).

Consideration of the size-partitioning of Fe and Th within the dissolved phase provides another constraint on the pathways these elements take after being released by dust. This investigation was also used as an opportunity to determine whether $^{232}\text{Th}$ and $^{230}\text{Th}$ have coherent speciation, as assumed for the $^{232}\text{Th}$ flux method. Fig. 6 presents these results based on measurements of ultra-filtered seawater from HOE-PhoR-II in September 2013. We define colloidal Th as dissolved (<0.45 μm) minus soluble (<10 kDa). Of the measured dissolved Th, 8–25% was found in the colloidal phase (0.45 μm – 10 kDa ∼ 0.01 μm). The total Th recovery during ultrafiltration was nearly complete (88–100%), implying that this 8–25% of dissolved Th was indeed colloidal in size, not an artifact of Th sorption/loss to the ultrafiltration system. Furthermore, at least at 15 m, 130 m (DCM), and 1000 m, the colloidal percentages for $^{232}\text{Th}$ and $^{230}\text{Th}$ agreed within the uncertainty of the measurements. This result implies coherent speciation of these thorium isotopes despite very different sources, and it supports the use of $^{236}\text{Th}$ as a tracer for $^{232}\text{Th}$ removal. Coherent speciation is also supported by previous measurements of the $^{232}\text{Th}/^{230}\text{Th}$ ratio of filtered (<0.2 μm) and ultrafiltered (<1 kDa) solutions from the Mediterranean Sea (Roy-Barman et al., 2002).

The role of colloids in Th scavenging has much history and deserves a few words of context. Early models of scavenging inferred that Th likely goes through a colloidal intermediate before being scavenged by larger, sinking particles (Honeyman et al., 1988; Honeyman and Santschi, 1989). Subsequent attempts at measuring colloidal Th focused largely on $^{234}\text{Th}$ (see review by (Guo and Santschi, 2007)), in part due to its use in quantifying organic matter export. A generalization might be made that outside of the coastal ocean, colloidal $^{234}\text{Th}$ was found to be a relatively small (~15%) proportion of the total dissolved (e.g., (Moran and Buesseler, 1992; Huh and Prahl, 1995; Guo et al., 1997)), which is also consistent with our $^{230}\text{Th}$ and $^{232}\text{Th}$ results. Recent observations from the North Atlantic
Hayes et al., 2015b), however, observed scavenging characteristics consistent with a strong role for Th colloids as predicted by the “colloidal pumping hypothesis” of Honeyman and Santschi (1989), even at open-ocean particle concentrations of <10 µg/kg seawater. Further observations on the geographic distribution of colloidal Th are clearly warranted.

Our paired observations of Th and Fe size partitioning nonetheless provide additional information on their physicochemical speciation in a comparative sense. Dissolved Fe has a much higher colloidal content at ALOHA than Th (Fig. 6). Above the DCM, dissolved Fe can be >50% colloidal. In the deeper water column, to 1.5 km depth, colloidal Fe is relatively constant at 40% (with the exception of one sample <10% colloidal at 650 m). Since Fe and $^{232}$Th are apparently solubilized from dust with equal fractional solubility, this difference in size-speciation is likely due to the selective uptake or complexation of Fe by organic substrates. Ligands, in the form of macromolecular organic molecules or organic colloidal particles, most likely complex Fe released from dust quite rapidly in the upper water column (Mendez et al., 2010; Bressac and Guieu, 2013). We hypothesize that organic Fe-binding ligands are predominantly responsible for converting such a large percentage of dissolved Fe to colloidal size. The inorganic speciation of Th in seawater is largely hydroxo- complexes (Santschi et al., 2006). Other similarly hydrolyzable metals such as Al and Ti do not have significant colloidal components (Dammhäuser and Croot, 2012).

Similar to Al and Ti, the abundance of colloidal ligands (>10 kDa) with an affinity to complex Th must also be small compared to the source of dissolved Th from dust. This finding does not necessarily contradict previous evidence for significant organic complexation of Th in seawater (Santschi et al., 2006). It does require, however, that any significant Th complexation is done by small (<10 nm), low-molecular weight organic molecules, at least in the subtropical North Pacific.

Greater uptake of Fe into the colloidal phase is another piece of evidence that suggests that dissolved Fe is cycled.
the euphotic zone. Dividing the integrated dissolved inventories by these residence times gives our estimate of the inventory of dissolved around 500 m. This pattern reflects that, at these times, dissolved inventories increase nearly linearly with integration depth slightly more quickly than the increase in Th residence time. Interestingly, in July 2012, the dissolved Th flux decreased with integration depth, reflecting that the Th residence time increased more quickly than the dissolved Th inventory, essentially because the mixed layer 230Th concentrations were exceptionally low at this time. Estimated 232Th fluxes are clearly quite sensitive to short-term variability in scavenging rates. We suggest further time-series analysis along with modeling efforts that contain circulation and realistic particle fluxes to determine more quantitatively the sensitivities involved in calculating dissolved 232Th fluxes during moderate changes in scavenging rates and dust input.

The three flux profiles converge around 1000 m depth. This is encouraging that over longer integration times, 10–15 years in this case, we estimate consistent lithogenic metal fluxes at multiple time points. Using Eq. (1), the dissolved 232Th fluxes are simply converted to dust-dissolved Fe fluxes, using SFe/Th = 1 and (Fe/Th)1.5 km = 11.040 mol/mol, shown in the second x-axis in Fig. 7B. The depth profiles of dissolved Fe concentrations from the same sampling campaigns are shown in Fig. 7C (Fitzsimmons et al., in press). Finally, using Eq. (2), by integrating Fe inventories and dividing by the dust-dissolved Fe fluxes, we estimate the residence time of dissolved Fe, as a function of integrated depth in Fig. 7D.

In the upper 250 m, the residence time of dissolved Fe is 6 months to 1 year, again assuming that the sole source of Fe to the surface ocean at Station ALOHA is aerosol dust deposition. This range agrees well with the 6 month residence time estimated previously at Station ALOHA (Boyle et al., 2005), and with other estimates of surface ocean dissolved Fe residence times from the Atlantic based on measured Fe concentrations and assumptions about soluble aerosol deposition (Jickells, 1999; Bergquist and Boyle, 2006; Ussher et al., 2013). With such fast turnover times, dissolved Fe concentrations in surface waters can be expected to vary on monthly to yearly timescales with changes in the seasonal input of dust from Asia. This is in fact exactly what was observed over the HOT and HOE time-series (Fitzsimmons et al., in press).

Available aerosol data suggest that Asian dust transport over the North Pacific had no significant long-term trend from 1981 to 2000 (Prospero et al., 2003) and perhaps a 6% decline over the past 10 years (Hyslop et al., 2013). Because of a nearly immediate impact on surface water Fe concentrations and the associated ecological consequences, it is important to monitor future changes in Fe sources. Sources such as Asian desert dust in our changing climate may vary independently of other Fe sources such as combustion aerosols.

As one integrates further from 250 to 1500 m, while the dissolved Fe fluxes change only moderately, the dissolved Fe residence times increase quickly to about 10 years at 1500 m depth. This is due to the large increase in Fe concentrations at these depths due to remineralization of Fe from sinking organic material and some portion of Fe accumulated and transported to ALOHA laterally via deep ocean circulation. There is potentially additional input of Fe at ~1 km depth due to Loihi hydrothermal activity. Additional lateral sources would cause our dust-based dissolved Fe residence time to be an overestimate, implying even faster timescales of Fe removal. On the other hand, as discussed in the next section, the 10 year Fe residence time at 1500 m could as well be an underestimate, if the geochemical cycles of Th and Fe become decoupled at greater depths where dust dissolution is no longer the most significant source of dissolved Fe.

4.5. Iron residence times

Using the 2012–2013 230Th profile data, we extend our calculations for Th residence time down to 1.5 km water depth in Fig. 7A. The average residence time for the depth zone between the surface and the DCM is 1–2 years. The Th residence times increase nearly linearly with integration depth to 14 years for the average residence time between the surface and 1.5 km. We do not plot integrated values shallower than the DCM (~120 m) on the assumption that steady-state Th scavenging may not apply under the conditions of stronger mixing and organic matter export within the euphotic zone. Dividing the integrated dissolved 232Th inventories by these residence times gives our estimate of dissolved 232Th flux, as a function of integration depth, in Fig. 7B.

In June and Sept. 2013, the dissolved 232Th flux increased with integration depth and began to level-off around 500 m. This pattern reflects that, at these times, the inventory of dissolved 232Th increased with integration depth slightly more quickly than the increase in Th residence time with depth. Interestingly, in July 2012, the dissolved 232Th flux decreased with integration depth, reflecting that the Th residence time increased more quickly than the dissolved 232Th inventory, essentially because the mixed layer 230Th concentrations were exceptionally low at this time. Estimated 232Th fluxes are clearly quite sensitive to short-term variability in scavenging rates. We suggest further time-series analysis along with modeling efforts that contain circulation and realistic particle fluxes...
4.6. Fe and Th decoupling in the deep ocean

Our focus on the upper water column stems from our motivation to understand trace metal cycling due to aerosol deposition and export production. We can extend our analysis of Fe and Th into the deep ocean (4.5 km water depth at Station ALOHA) to learn about the geochemistry of these elements over decadal-to-centennial timescales. In Fig. 8, we compiled available deep profiles from Station ALOHA for dissolved Fe (Boyle et al., 2005; Morton, 2010; Fitzsimmons et al., in press) and dissolved $^{232}$Th and $^{230}$Th (this study; Roy-Barman et al., 1996).

Variability in dissolved Fe at 1–1.5 km is clearly apparent, likely due to hydrothermal inputs. Below 1.5 km depth, Fe, $^{232}$Th, and $^{236}$Th display relatively constant profile shapes, at least during the sparse sampling dates. From 2 km depth to the bottom, dissolved Fe is nearly constant or slightly decreases with depth to about 0.4 nmol/kg, while dissolved $^{232}$Th actually increases with depth from 50 to 180 fmol/kg below 3000 m. This divergence in profile shape already suggests a decoupling of the behavior of these elements in the deep ocean.

The deep ocean appears to contain an additional source for $^{232}$Th. This source is potentially related to resuspension of diagenetically-altered sediments at the seafloor (Okubo et al., 2012; Hayes et al., 2013a). The bottom-increase in $^{232}$Th begins nearly 2 km above the seafloor, much higher than typical benthic vertical mixed layers (50–100 m) (Richards, 1990). This phenomenon, as observed with km-scale nepheloid layers (McCave, 1986), suggests that the $^{232}$Th at abyssal depths of Station ALOHA is being mixed in laterally from locations where isopycnals impinge on surrounding bathymetry.

Also related to bottom sediment resuspension, the July 2012 profile of $^{230}$Th displays a negative concentration anomaly, or deficit of $^{230}$Th, with respect to the linear profile near the seafloor (Fig. 8C). This bottom $^{230}$Th deficit is indicative of enhanced bottom scavenging as observed in
It is non-intuitive that a bottom layer where the scavenging removal of Th is enhanced compared to the overlying water column would also be a strong source of $^{232}$Th. The resuspension of bottom sediments may produce such a strong release of $^{232}$Th that this source more than compensates for enhanced scavenging. Another contributing factor may be that the resuspended thorium could have a much higher $^{232}$Th/$^{230}$Th ratio than the water column due to age-decay of $^{230}$Th in the sediments.

Dissolved Fe, on the other hand, appears unaffected by bottom processes, displaying only a slight decrease in concentration with depth (Fig. 8A). The slight decrease with depth may be related to scavenging of Fe as deep water masses age (Bruland et al., 1994). If we extend our integrated residence time approach to the deep Fe profile at Station ALOHA (Fig. 9), we derive a whole ocean residence for dissolved Fe of only 30 years. This is significantly shorter than the 100–300 year estimates of the ocean residence time for dissolved Fe based on deepwater scavenging (Bruland et al., 1994; Bergquist and Boyle, 2006). This discrepancy must arise because the deep ocean source of $^{232}$Th does not add dissolved Fe to the water column at a crustal ratio, unlike what occurs during near-surface dust dissolution. Thus, the $^{232}$Th flux method for Fe residence times probably should not be extended to the deep ocean.

The question remains: how is an element like Th, a trace component of continental material, added to the deep ocean without a simultaneous release of a major crustal element like Fe? The answer is likely related to solubility. Dissolved Fe in the deep central North Pacific at $\sim$0.5 nmol/kg has been found to be at near solubility equilibrium with Fe(III) hydroxide (Kuma et al., 2003; Kitayama et al., 2009). These studies determine Fe(III)
solubility by adding gamma-emitter $^{59}$Fe(III) to filtered seawater, allowing the solutions to come to solubility equilibrium with Fe(III) hydroxide over several weeks, subsequently filtering the seawater and then counting the $^{59}$Fe gamma-activity on the final filtrate. The observed ~0.5 nmol/kg solubility is elevated over Fe solubility in inorganic seawater because of the presence of organic ligands (Liu and Millero, 2002). Thus, since the deep Pacific is in a near saturation state, dissolved Fe can no longer be expected to increase, even in the presence of increasing Th concentrations.

A problem with this argument is that electrochemically-determined Fe ligand concentrations at Station ALOHA are up to 2 nmol/kg, well in excess of dissolved Fe concentrations (Rue and Bruland, 1995), as found in most of the world ocean (Gledhill and Buck, 2012). However, it may not be kinetically appropriate to compare Fe ligand concentrations directly with seawater solubility. In either estimation, deepwater dissolved Fe is at least close to (within the same order of magnitude) our best estimates of Fe solubility.

While much less in known about Th solubility in seawater, our large underestimate of Fe residence time in the deep ocean implies that the deep North Pacific, with Th at ~180 fmol/kg, is below Th solubility equilibrium. Near-sea water pH and ionic strength, the solubility of Th(IV) hydroxide may be as high as 0.5–1 nmol/kg, compared to 1 fmol/kg for crystalline ThO$_2$, due to the amorphous nature of Th(OH)$_4$ solids (Neck et al., 2003). Also, electrochemical methods suggest organic Th ligands exist at nanomolar concentrations (Hirose, 2004). Despite our finding of low colloidal Th content, organically-bound Th could of course be present at Station ALOHA if the complexes are smaller than ~10 nm. We advocate direct measurements of Th solubility in seawater, perhaps using radio-tracer additions with similar protocols as developed for Fe (Kuma et al., 1996; Schlosser and Crook, 2008), to confirm that Th exists in the deep ocean at much less than its equilibrium solubility. This would explain the fact that dissolved Th concentrations continue to grow from lithogenic sources in the deep North Pacific, where Fe concentrations become fixed by a solubility limit.

5. CONCLUSIONS

Using time-series data from the North Pacific, this study finds variability in surface Fe and $^{232}$Th concentrations consistent with a source from Asian dust. The dust source likely has a relative Fe/Th fractional solubility close to 1. The application of $^{230}$Th scavenging rates to $^{232}$Th inventories allows the accurate evaluation of the flux of dissolved metals from dust in the remote surface ocean. The source flux of dissolved Fe, derived from $^{230}$Th-based timescales, suggests that dissolved Fe in the upper 250 m is turning over in 1 year or less. A compelling implication of this result is that Fe delivery to phytoplankton can be expected to vary with seasonal-to-interannual changes in dust delivery from Asia. Continued monitoring of Fe-dependent biological processes, such as nitrogen fixation, are crucial to anticipate the consequences of changing land-use and/or industrial processes that may significantly affect eolian sources of Fe to the North Pacific.

In addition, by comparing Fe and Th size-partitioning, we find evidence that colloidal Fe may be of predominantly organic composition in the subtropical North Pacific. We also hypothesize that iron reaches a solubility limit in the deep sea (>2 km) while Th does not. While less controversial for Th, this result questions the relevance of “excess” Fe ligands in the deep sea. Overall, however, the kinetic box model approach to tracing dust-derived elements (Fig. 1) appears well-suited in the upper water column (~250 m).

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APPENDIX A. SUPPLEMENTARY DATA

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.gca.2015.07.019.

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