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

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11 **Abstract**

12 The role of iron as a limiting micronutrient motivates an effort to understand the supply and
13 removal of lithogenic trace metals in the ocean. The long-lived thorium isotopes (²³²Th and
14 ²³⁰Th) in seawater can be used to quantify the input of lithogenic metals attributable to the partial
15 dissolution of aerosol dust. Thus, Th can help in disentangling the Fe cycle by providing an
16 estimate of its ultimate supply and turnover rate. Here we present time-series (1994-2014) data
17 on thorium isotopes and iron concentrations in seawater from the Hawaii Ocean Time-series
18 station ALOHA. By comparing Th-based dissolved Fe fluxes with measured dissolved Fe
19 inventories, we derive Fe residence times of 6-12 months for the surface ocean. Therefore, Fe
20 inventories in the surface ocean are sensitive to seasonal changes in dust input. Ultrafiltration
21 results also reveal that Th has a much lower colloidal content than Fe, implicating a predominant
22 role for sub-micron organic ligands specific to Fe, or possibly inorganic Fe colloids. In the deep
23 ocean, Fe approaches a solubility limit while Th, surprisingly, is continually leached from
24 lithogenic particles. This distinction in solubility suggests Th is not a good tracer for Fe in the
25 deep (>2 km) ocean. While uncovering divergent behavior of these elements in the water
26 column, this study finds that dissolved Th flux is a suitable proxy for the supply of Fe from dust
27 in the remote surface ocean.

28 **1. Introduction**

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

39 In this study, we assess the utility of thorium isotopes in seawater to provide rate
40 information on the Fe cycle. In addition to producing a measure of total dust flux to the ocean
41 (Deng et al., 2014; Hsieh et al., 2011), by pairing ^{232}Th , sourced from dust, with radiogenic ^{230}Th
42 (or ^{234}Th) that provides a timescale of thorium flux, one can make quantitative estimates of the
43 trace metals released by dust dissolution (Hayes et al., 2013a). Our study site is the Hawaii
44 Ocean Time-series station ALOHA (22° 45' N, 158° W) (Church et al., 2013; Karl and Lukas,
45 1996) in the subtropical North Pacific, where Asian dust is deposited in spring (Boyle et al.,
46 2005; Hyslop et al., 2013; Prospero et al., 2003). Presenting time-series data spanning 20 yrs
47 (1994-2014), we demonstrate that the behaviors of Fe and Th in seawater are consistent with a
48 variable dust source to the surface ocean. Thorium-based fluxes indicate that the residence time
49 of dissolved Fe in the upper 125 m of the water column is less than one year. In the sub-surface

50 ocean (>250 m), the thorium and iron cycles begin to diverge considerably. These divergences
 51 reveal new insights into the marine geochemistry of these elements.

52 **2. Background**

53 *2.1 Finding the timescale: thorium removal*

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

62 Thus by comparing the amount of ^{230}Th that remains in seawater to the amount produced
 63 by U decay, one can calculate a removal timescale (Eq. 1, Fig. 1), or residence time (τ), of
 64 thorium in seawater. This technique is analogous to that used with a more commonly used flux
 65 tracer, the shorter-lived ^{234}Th (half-life 24.1 days). By the same principles, using its production
 66 rate from parent isotope ^{238}U , ^{234}Th inventories can also be used to determine the scavenging rate
 67 of Th in seawater (Buesseler et al., 1992; Coale and Bruland, 1985).

$$68 \quad \tau_{Th}(z) = \frac{\int_0^z {}^{230}\text{Th} dz}{\int_0^z {}^{234}\text{U} * \lambda_{230} dz} \quad \text{Eq. 1}$$

69 To meet the requirements of a steady-state assumption between source and removal
 70 terms, we calculate thorium residence times in an integrated sense, from the surface to a
 71 particular depth. Thus as one integrates deeper into the water column, the ^{230}Th inventories
 72 reflect longer timescales of removal. Residence times calculated in this way also neglect

73 dispersal fluxes by ocean circulation. Lateral gradients in oceanic ^{230}Th concentrations are
 74 generally small (Hayes et al., 2014), while large vertical gradients may make vertical fluxes
 75 significant, for instance due to upwelling (Luo et al., 1995).

76 2.2 Finding the source: lithogenic metal fluxes

77 The dominant isotope of seawater thorium is primordial and long-lived (half-life $14.1 \times$
 78 10^9 yrs) ^{232}Th . It is added to the ocean only through the partial dissolution of continental
 79 material, which in the context of station ALOHA we consider to be primarily aerosol dust. As
 80 scavenging tendencies are characteristic of all isotopes of an element, once in the water column,
 81 ^{232}Th undergoes scavenging removal (Fig. 1) assumedly at the same rate, i.e. with the same
 82 residence time, as ^{230}Th (or ^{234}Th). Assuming a steady-state for Th concentrations, with
 83 knowledge of the Th residence time, derived from ^{230}Th , one can calculate the flux of dust-
 84 derived ^{232}Th necessary to support the observed ^{232}Th inventory (Eq. 2). As in calculating
 85 thorium residence times, the dissolved ^{232}Th flux derived is reflective of the integrated depth
 86 zone, rather than at a particular depth. More details on ^{232}Th flux calculations are reported by
 87 Hayes et al. (2013a).

$$88 \quad {}^{232}\text{Th flux}(z) = \frac{\int_0^z {}^{232}\text{Th} dz}{\tau_{\text{Th}}(z)} \quad \text{Eq. 2}$$

89 In comparison to the relative simplicity of the supply and removal terms in the thorium
 90 cycle, seawater iron cycling has many more terms to consider. These include biological uptake,
 91 remineralization, redox chemistry, anthropogenic or hydrothermal sources, in addition to supply
 92 by dust and removal by scavenging (Fig. 1). Scavenging of Fe also occurs but at a different rate
 93 than that of Th. The utility of this element pair is their common source from dust. We propose
 94 using dissolved ^{232}Th flux as a proxy for the Fe released during dust dissolution. This can be

95 done with knowledge of the Fe/Th ratio in the dust and the relative fractional solubility of the
 96 two elements ($S_{\text{Fe/Th}}$, Eq. 3).

$$97 \quad \text{Dust-dissolved Fe flux} = \text{dissolved } ^{232}\text{Th flux} \times (\text{Fe/Th})_{\text{dust}} \times S_{\text{Fe/Th}} \quad \text{Eq. 3}$$

98 By weight, the Asian desert dust which undergoes long-range transport over the North
 99 Pacific contains ^{232}Th at 14.3 ± 0.8 ppm, based on fine grained ($<8 \mu\text{m}$) source materials
 100 (McGee, 2009; Serno et al., 2014), and Fe at 3.8 ± 0.4 %, based on a literature compilation by
 101 Mahowald et al. (2005). Therefore, we assume the Fe/Th ratio in dust at station ALOHA of 2660
 102 ± 320 g/g or $11,040 \pm 1450$ mol/mol. These ratios are close to the average for the upper
 103 continental crust of $\text{Fe/Th} = 3271 \text{ g/g} = 13,553 \text{ mol/mol}$ (Taylor and McLennan, 1995).

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

109 *2.3 Iron residence times*

110 We cannot rule out significant marine Fe sources by anthropogenic (e.g., derived from
 111 fossil fuel combustion) aerosols, continental margin sediments, or deep-sea hydrothermal vents.
 112 We can, however, entertain the thought that if dust were the only Fe source to the water column,
 113 the comparison between measured dissolved Fe inventories to the source (dust-dissolved Fe flux)
 114 would produce a measure of the turnover rate or residence time of dissolved Fe in seawater (Eq.
 115 4). This residence time again represents the residence time within the integrated water column.
 116 Additional sources of Fe, such as combustion aerosols or hydrothermal fluids, would cause the

117 dust-based Fe residence time to be an overestimate. Relevant to iron cycling, this residence time
118 provides a rough timescale over which one can expect Fe concentration to vary as a result of
119 variation in sources, such as springtime Asian dust events (Boyle et al., 2005).

$$120 \quad \text{Dissolved Fe residence time} = \text{Fe inventory} \div \text{dust-dissolved Fe flux} \quad \text{Eq. 4}$$

121 **3. Materials and Methods**

122

123 *3.1 Sample collection during 2012-2014*

124

125 Samples were collected on several cruises on the R/V *Kilo Moana*, led by the Center for

126 Microbial Oceanography: Research and Education (C-MORE), to station ALOHA in July-

127 September 2012 (HOE-DYLAN), May-June 2013 (HOE-PhoR-I), September 2013 (HOE-PhoR-

128 II) and March 2014 (HOE-BOE-I). Depth profiles for $^{230}\text{Th}/^{232}\text{Th}$ analysis were collected from

129 the ship's Niskin bottle rosette, filtered with a 0.45 μm Acropak cartridge filter, and acidified to
130 pH 1.8 with Savillex-distilled 6 M HCl.

131 Filtered surface seawater (0.4 μm) was collected for ^{232}Th (which requires smaller

132 volumes than for ^{230}Th), as well as for dissolved Fe, using the trace-metal clean MITESS

133 sampler (Bell et al., 2002) at near daily time intervals on the 2012-2013 C-MORE cruises.

134 MITESS collection methods, including "Vane" sampling for Fe depth profiles, on the HOE

135 campaigns are discussed fully by Fitzsimmons et al. (submitted). Within 3 hours of collection,

136 the seawater was filtered using 0.4 μm polycarbonate track etch filters (PCTE, Whatman).

137 Particulate samples were immediately frozen, and dissolved filtrates were acidified to pH 2 with

138 trace metal clean HCl. The filters used for filtering MITESS water were analyzed for particulate

139 Fe and ^{232}Th (representing on average 0.7 liters of seawater).

140 On HOE-PhoR-II, cross flow filtration was performed to assess colloidal $^{232}\text{Th}/^{230}\text{Th}$

141 using protocols developed to study colloidal Fe (Fitzsimmons and Boyle, 2014a). Seawater was

142 pre-filtered at 0.45 μm and, within 1-2 hours, pumped over a Millipore Pellicon XL filter made
143 of regenerated cellulose with a nominal molecular weight cutoff of 10 kDa, roughly equivalent to
144 an effective pore size of 10 nanometers. Both permeate and retentate fractions were analyzed to
145 determine any loss of Th by adsorption, which turned out to be minimal (88-100% dissolved Th
146 recovery).

147 *3.2 Hawaii Ocean Time-series (HOT) seawater*

148 Seawater samples, typically 0.5 liter size, have been collected during the HOT program
149 for trace metal analysis at MIT periodically since 1997. Most of these samples were collected as
150 unfiltered water using the MITESS sampler (Bell et al., 2002) and subsequently preserved by
151 acidification to pH 2 with HCl. Further sampling details are given by Boyle et al. (2005). We
152 also make use of literature seawater $^{232}\text{Th}/^{230}\text{Th}$ data, collected at station ALOHA in September
153 1994 (HOT-57), reported by Roy-Barman et al. (1996).

154 *3.3 Thorium and iron analyses*

155 Dissolved ^{230}Th concentrations at station ALOHA are as low as 10^{-18} moles per kilogram
156 seawater ($10^{-18} \text{ mol } ^{230}\text{Th} = 0.1746 \mu\text{Bq}$). Therefore, for measurement by inductively-coupled
157 plasma mass spectrometry (ICP-MS), 4-5 liter water samples are required. Thorium
158 concentrations were determined by isotope dilution by spiking with ^{229}Th (not present in natural
159 seawater). Sample preparation (pre-concentration, acid digestion, and chromatographic
160 purification) was performed using published methods (Anderson et al., 2012; Auro et al., 2012).
161 A portion of the ^{230}Th samples were prepared and analyzed at the Lamont-Doherty Earth
162 Observatory (L-DEO), using an Element XR single-collector ICP-MS. The remaining ^{230}Th
163 samples were prepared at the Massachusetts Institute of Technology (MIT) and analyzed using a

164 Neptune Plus multi-collector ICP-MS at Brown University. Th-232 was also analyzed in samples
165 prepared for ^{230}Th .

166 Analysis of ^{232}Th , at 10^{-15} mol or femtomoles per kg seawater, required smaller samples
167 (200-800 mL) and was measured on archive HOT and HOE samples for which sample volume
168 did not allow ^{230}Th determination. While not as prone to contamination as some other trace
169 elements, clean lab techniques were required to produce blanks that were consistent and low
170 enough to allow detection of the relatively small sample size of ~20-40 femtomoles ^{232}Th .
171 Therefore, modifications of the cited procedures for Th analysis (Anderson et al., 2012; Auro et
172 al., 2012) were made. Instead of co-precipitation with added Fe, pre-concentration of ^{232}Th was
173 achieved using magnesium hydroxide co-precipitation, such as that described for Pb by Reuer et
174 al. (2003). Thorium was purified using a smaller amount (100 μl rather than 1 ml) of anion-
175 exchange resin (AG1-X8) on columns fashioned from Teflon shrink-tubing. Samples were
176 loaded onto AG1-X8 resin in 8 M HNO_3 and Th was eluted with 6 M HCl (instead of 12 M HCl,
177 to reduce acid blank), following Edwards et al. (1987). Blank determinations were made on 125
178 mL aliquots of acidified seawater samples whose ^{232}Th content had been determined during
179 previous ^{230}Th analysis. The mean procedural blank ($n = 6$) was 3.5 ± 1.6 fmol ^{232}Th , resulting in
180 a detection limit of 4.8 fmol ^{232}Th . Samples for seawater ^{232}Th were prepared and analyzed at
181 MIT, using a Micromass IsoProbe multi-collector ICP-MS.

182 In this study, we refer to measured trace metal concentrations as dissolved (filtered at 0.4
183 or 0.45 μm), particulate (>0.4 μm), or total (acidified unfiltered water). The “total”
184 concentrations in this sense are sometimes referred to as “total dissolvable”, allowing for the
185 possibility that some forms of Th are not preserved by acidification or collected with co-
186 precipitation. Since our goal in interpreting seawater ^{230}Th concentrations is to determine

187 scavenging rates based on uranium decay, we made small (0-10%) corrections for the dissolved
188 ^{230}Th released from dust (or lithogenic material in general). This correction is based on measured
189 dissolved ^{232}Th and a lithogenic $^{230}\text{Th}/^{232}\text{Th}$ mole ratio of 4×10^{-6} (Roy-Barman et al., 2009).
190 The corrected dissolved ^{230}Th values are denoted as “xs”.

191 Particulate ^{232}Th and particulate Fe, were analyzed at Florida State University by total
192 digestion of the filter samples and subsequent analysis by ICP-MS, using slightly modified
193 versions of published protocols (Ho et al., 2011; Morton et al., 2013; Upadhyay et al., 2009). In
194 brief, samples were microwaved (CEM MARS Xpress) for 40 minutes at 180°C with HNO_3 and
195 H_2O_2 (to digest the organic and less refractory biogenic and authigenic components) and HF (to
196 digest the more refractory lithogenic components). The detection limit (based on 3 standard
197 deviations of the digested acid blanks) for particulate ^{232}Th was 8 fmol/L (n=19) and the
198 particulate Fe detection limit was 0.2 nmol/L (n=21). Dissolved Fe was measured by isotope
199 dilution after pre-concentration onto nitrilotriacetate resin on the Micromass IsoProbe ICP-MS at
200 MIT (Lee et al., 2011). Further details on Fe analyses are discussed by Fitzsimmons et al.
201 (submitted).

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

203 **4. Results and Discussion**

204 *4.1 ^{230}Th - ^{232}Th depth profiles to 1.5 km*

205
206
207 We focus first on the 2012-2013 thorium isotope depth profiles in the upper 1.5 km of the
208 water column for a sense of the type of data used to calculate thorium fluxes (Fig. 2). High
209 resolution depth profiles were analyzed in late July 2012, early June 2013 and late September
210 2013. The mixed layer depths during these sampling casts (based on 0.125 kg/m^3 density change)

211 were 54, 33 and 53 m, respectively, and below 100 m these profiles displayed little
212 distinguishing hydrography (Figs. 2C, 2D, 2E).

213 For dissolved ^{232}Th (Fig. 2A), there were increased concentrations near the surface,
214 minimum concentrations at the depth of maximum chlorophyll concentration (the DCM, ~120-
215 140 m), and a relatively constant local concentration maximum at 500-600 m depth. At
216 intermediate depths (900-1200 m), each profile exhibited smooth variations in concentration but
217 concentrations at the different sampling dates vary by up to 30%.

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

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

229 Scavenged ^{232}Th may be partially released through remineralization of particles in
230 mesopelagic depths (300-500 m). Thus remineralization may be responsible for some of the
231 subsurface ^{232}Th maxima at 400-600 m depth. In support of this view, this depth range coincides
232 with a rapid increase in phosphate concentration and apparent oxygen utilization, as inferred
233 from HOT climatology (<http://hahana.soest.hawaii.edu/hot/trends/trends.html>). On the other

234 hand, the attenuation of particulate organic carbon at station ALOHA is most intense at
235 shallower depths, between 100 and 200 m (Bishop and Wood, 2008).

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

241 The variability in ^{232}Th concentration at intermediate depths (900-1400 m) could be due
242 to the effect of hydrothermal activity at the nearby Loihi seamount. The iron oxide particles
243 associated with hydrothermal plumes strongly scavenge Th, and depleted deep-sea Th
244 concentrations have been observed up to 1400 km away from a vent site in the Atlantic (Hayes et
245 al. 2014). We note however, that while variability in ^{232}Th could suggest hydrothermal
246 scavenging, intriguingly, this effect is apparently weak enough to not significantly perturb the
247 near-linear ^{230}Th profiles (Fig. 2). Time-variability in the influence of the Loihi hydrothermal
248 system on trace metals at ALOHA is discussed more fully by Fitzsimmons et al. (submitted).

249 The ^{230}Th profiles also displayed interesting temporal variations. The theory of reversible
250 scavenging contends that a steady-state is achieved between thorium adsorption and desorption
251 on uniform particles that settle at a constant rate (Bacon and Anderson, 1982). Under these
252 assumptions, one expects ^{230}Th concentrations to increase linearly with depth with a boundary
253 condition of zero concentration at the surface. While the observed depth profiles are essentially
254 linear (Fig. 2B), it appears that mixing at the surface homogenizes ^{230}Th concentrations to some
255 depth. Interestingly, the layer of relatively homogeneous ^{230}Th extends deeper than the density-
256 defined mixed layer (30-50 m), down to the deep chlorophyll maximum (Fig. 2). This

257 phenomenon is worthy of future time-series study. Potentially a remnant of deep winter mixed
258 layers (< 100 m), the homogeneous surface ^{230}Th layer could also represent some combination
259 of vertical mixing and enhanced scavenging related to export of organic matter from the euphotic
260 zone.

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

268 *4.2 Surface thorium residence times*

269 Residence times of dissolved ^{230}Th as described in section 2.1 using the 2012-2014
270 results are presented in Figure 3. In this assessment, we integrate production due to ^{234}U decay
271 (based on salinity) and the measured ^{230}Th inventory to 150 m depth. This allows comparison to
272 Th residence times calculated on the basis of $^{234}\text{Th}:$ ^{238}U disequilibrium established by previous
273 work at station ALOHA, during April 1999-March 2000 (Benitez-Nelson et al., 2001) and June-
274 July 2008 (Buesseler et al., 2009). The ^{234}Th results differ slightly from the approach used here
275 for dissolved ^{230}Th since the ^{234}Th fluxes are calculated using unfiltered seawater. Since
276 adsorbed ^{230}Th concentrations are on the order of ~10-20% of total ^{230}Th (Roy-Barman et al.,
277 1996), residence times based on total ^{234}Th can be expected to be up to 10-20% lower than those
278 based on the dissolved phase only.

280 We also assessed the influence of vertical mixing on surface ^{230}Th inventories, which
281 could influence the derived residence time. Assuming a vertical mixing coefficient (K_v) of 10^{-5}
282 m^2/s (Charette et al., 2013), using a second-order polynomial regression of the ^{230}Th depth
283 profiles (above 250 m), we can calculate the vertical mixing rate of ^{230}Th , as $K_v \times d^2\text{Th}/dz^2$. The
284 results indicate that vertical mixing adds ^{230}Th to surface water at a rate of less than 5% of
285 production due to ^{234}U decay. Therefore we can assume that vertical mixing does not
286 significantly affect the ^{230}Th residence time estimates at Station ALOHA.

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

293 The concept of “residence time” used here is based on a steady-state assumption for
294 sources and sinks. Therefore with a residence time of ~ 2 years, one would not expect significant
295 variation in the removal timescale over a period of months. However, the range in observed Th
296 residence times for Station ALOHA indicates that this steady-state assumption is not quite
297 correct. More precisely, the steady-state for scavenging removal of Th appears to hold within a
298 factor of 2-3. The range in removal timescales observed based on ^{230}Th is similar to that based on
299 ^{234}Th . Thus, it seems the rate of thorium scavenging can change dynamically at Station ALOHA
300 possibly related to export pulses, but the data are consistent with a long-term average thorium
301 residence time of 2 ± 1 years in the upper 150 m.

302 *4.3 Surface ^{232}Th concentrations*

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

308 Collected during a series of cruises in summer 2012 (HOE-DYLAN), daily-scale samples
309 of 250 mL were analyzed for dissolved and particulate ^{232}Th . Sample size required combining
310 the samples from 2-4 days for dissolved ^{232}Th , contributing to some degree of smoothing.
311 Dissolved concentrations ranged from 45-90 fmol/kg (Fig. 4C). Particulate ^{232}Th , although
312 measured at a higher, daily resolution, had a higher range of variability, from 10-290 fmol/kg. Of
313 the total seawater ^{232}Th (dissolved + particulate) during HOE-DYLAN, on average 42% was in
314 the particulate phase (range 26-66%). This fraction particulate is higher than that for ^{230}Th
315 (~15%, Roy-Barman et al., 1996) since particulate ^{232}Th represents both adsorbed Th and
316 structural Th in mineral dust.

317 The decadal time-series observations (1994-2014) of total ^{232}Th (Fig. 4A) exhibit a range
318 in concentration (~50-300 fmol/kg) that is consistent with the higher frequency observations of
319 particulate Th in 2012-2013. Since most of the data fall within the range of 50-150 fmol/kg, we
320 are not fully confident in the five observations of elevated concentrations (150-300 fmol/kg)
321 observed in 1994, 1998, and 1999 samples. In particular, the 1998 and 1999 samples were
322 collected using a moored, rather than ship-based, MITESS sampler in which bottles were filled
323 with 1 M HCl prior to filling with seawater. Mooring-collected water at times had higher Th
324 concentrations than ship-based sampling (Fig. 4) and thus the possibility of contamination during
325 sampling, sample storage, or sample analysis cannot be fully discounted. In fact, the 1994 results

326 from Roy-Barman et al. (1996) came from samples collected on the same Niskin bottle cast.
327 Spatial variability, related to mesoscale eddies, is another potential source of rapid changes in
328 surface ^{232}Th concentration. Conservatively excluding the elevated observations >150 fmol/kg,
329 no significant temporal term trend can be derived.

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

338 *4.4 Fe/Th ratio behavior in surface water and in colloidal content*

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

343 In the context of daily, monthly and decadal variability, it appears that the ratio of total
344 and particulate $\text{Fe}/^{232}\text{Th}$ tends to be at or above the dust-ratio of 11,040 mol/mol, while dissolved
345 $\text{Fe}/^{232}\text{Th}$ is at or below the dust-ratio (Fig. 5A & 5B). These observations are consistent with
346 input at the dust $\text{Fe}/^{232}\text{Th}$ ratio and a strong sink from biological uptake for Fe. Thus, the
347 dissolved phase is left depleted in Fe relative to ^{232}Th , while the particulate phase becomes
348 enriched in biogenic Fe. The total Fe/Th ratio often exceeds the dust ratio as well, possibly

349 because biogenic particulate Fe may be efficiently recycled and thus may reside in the surface
350 longer than particulate Th.

351 The partitioning between dissolved and total/particulate Fe/²³²Th centers around the dust-
352 ratio (Fig. 5C). We interpret this to mean that the relative fractional solubility of Fe and ²³²Th
353 ($S_{\text{Fe/Th}}$) is close to 1. An alternate interpretation would be that ²³²Th is more efficiently leached
354 from dust, leaving the particulate phase enriched in Fe/²³²Th and the dissolved phase depleted in
355 Fe/²³²Th. However, given the known ability for phytoplankton to efficiently utilize Fe from dust
356 sources (e.g., (Rubin et al., 2011)), the assumption of $S_{\text{Fe/Th}} = 1$ during dissolution followed by
357 rapid biological uptake of Fe seems more likely.

358 Consideration of the size-partitioning of Fe and Th within the dissolved phase provides
359 another constraint on the pathways these elements take after being released by dust. This
360 investigation was also used as an opportunity to determine whether ²³²Th and ²³⁰Th have
361 coherent speciation, as assumed for the ²³²Th flux method. Figure 6 presents these results based
362 on measurements of ultra-filtered seawater from HOE-PhoR-II in September 2013. We define
363 colloidal Th as dissolved (< 0.45 μm) minus soluble (< 10 kDa).

364 Of the measured dissolved Th, less than 25% was found in the colloidal phase (0.45 μm -
365 10 kDa \approx 0.01 μm). Furthermore, at least at 15 m, 130 m (DCM), and 1000 m, the colloidal
366 percentage for ²³²Th and ²³⁰Th agreed within the uncertainty of the measurements. This result
367 implies coherent speciation of these thorium isotopes despite very different sources and supports
368 the use of ²³⁰Th as a tracer for ²³²Th removal. This coherent speciation result agrees with
369 previous measurements of the ²³²Th/²³⁰Th ratio of filtered (< 0.2 μm) and ultrafiltered (< 1 kDa)
370 solutions from the Mediterranean Sea (Roy-Barman et al., 2002).

371 The role of colloids in Th scavenging has much history and deserves a few words of
372 context. Early models of scavenging inferred that Th likely goes through a colloidal intermediate
373 before being scavenged by larger, sinking particles (Honeyman et al., 1988; Honeyman and
374 Santschi, 1989). Subsequent attempts at measuring colloidal Th focused largely on ^{234}Th (see
375 review by (Guo and Santschi, 2007)), in part due to its use in quantifying organic matter export.
376 A generalization might be made that outside of the coastal ocean, colloidal ^{234}Th was found to be
377 relatively small ($\sim <15\%$) proportion of the total dissolved (e.g., (Guo et al., 1997; Huh and Prahl,
378 1995; Moran and Buesseler, 1992)), which is also consistent with our $^{230}\text{Th}/^{232}\text{Th}$ results. Recent
379 observations from the North Atlantic (Hayes et al., submitted), however, observed scavenging
380 characteristics consistent with a strong role for Th colloids as predicted by Honeyman and
381 Santschi (1989), even at open-ocean particle concentrations of $< 10 \mu\text{g}/\text{kg}$ seawater. Further
382 observations on the geographic distribution of colloidal Th are clearly warranted.

383 Our paired observations of Th and Fe size partitioning nonetheless provide additional
384 information on their physicochemical speciation in a comparative sense. Dissolved Fe has much
385 more colloidal content at ALOHA than Th (Fig. 6). Above the DCM, dissolved Fe can be $>50\%$
386 colloidal. In the deeper water column, to 1.5 km depth, colloidal Fe is relatively constant at 40%
387 (with the exception of one sample $< 10\%$ colloidal at 650 m). Since Fe and ^{232}Th are apparently
388 solubilized from dust with equal fractional solubility, this difference in size-speciation is most
389 likely also due to the selective uptake or complexation of Fe by organic substrates. Ligands, in
390 the form of macromolecular organic molecules or organic colloidal particles, most likely
391 complex Fe released from dust quite rapidly in the upper water column (Bressac and Guieu,
392 2013; Mendez et al., 2010). It is the size of these organic Fe-binding ligands that are thought to
393 convert such a large percentage of dissolved Fe to colloidal size, as other similarly hydrolyzable

394 metals such as Al and Ti do not have significant colloidal components (Dammshäuser and Croot,
395 2012).

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

402 Greater uptake of Fe into the colloidal phase is another piece of evidence that suggests
403 that dissolved Fe is cycled more rapidly than Th in the upper water column. The innovation of
404 the ^{232}Th flux method is our ability to be quantitative about the rates of Fe removal, which are
405 presented in the next section.

406 4.5 Iron residence times

407 Using the 2012-2013 Th profile data, we extend our calculations for Th residence time
408 down to 1.5 km water depth in Fig. 7A. Beginning at the 1-2 years residence times calculated by
409 integrating to the DCM, the Th residence times increase nearly linearly with integration depth to
410 14 years at 1.5 km. Dividing the integrated dissolved ^{232}Th inventories by these residence times
411 gives our estimate of dissolved ^{232}Th flux, as function of integration depth, in Fig. 7B.

412 In June and Sept. 2013, the dissolved ^{232}Th flux increased with integration depth and
413 begins to level-off around 500 m. This reflects that, at these times, the inventory of dissolved
414 ^{232}Th increased with integration depth slightly more quickly than the increase in Th residence
415 time with depth. Interestingly, in July 2012, the dissolved ^{232}Th flux decreased with integration
416 depth, reflecting that the Th residence time increased more quickly than the dissolved ^{232}Th

417 inventory, largely because the mixed layer ^{230}Th concentrations were exceptionally low at this
418 time. Estimated ^{232}Th fluxes are clearly quite sensitive to short-term variability in scavenging
419 rates. We suggest further time-series analysis along with modelling efforts that contain
420 circulation and realistic particle fluxes to determine more quantitatively the sensitivities involved
421 in calculating dissolved ^{232}Th fluxes during moderate changes in scavenging rates and dust input.

422 The three flux profiles converge around 1000 m depth. This is encouraging that over
423 longer integration times, 10-15 years in this case, we estimate consistent lithogenic metal fluxes
424 at multiple time points. Using Eq. 1, the dissolved ^{232}Th fluxes are simply converted to dust-
425 dissolved Fe fluxes, using $S_{\text{Fe/Th}} = 1$ and $(\text{Fe/Th})_{\text{dust}} = 11,040 \text{ mol/mol}$, shown in the second x-
426 axis in Fig. 7B. The depth profiles of dissolved Fe concentrations from the same sampling
427 campaigns are shown in Fig. 7C (Fitzsimmons et al., submitted). Finally, using Eq. 2, by
428 integrating Fe inventories and dividing by the dust-dissolved Fe fluxes, we estimate the residence
429 time of dissolved Fe, as a function of integrated depth in Fig. 7D.

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

438 Available aerosol data suggest that Asian dust transport over the North Pacific has no
439 significant trend from 1981 to 2000 (Prospero et al., 2003) and perhaps a 6% decline over the

440 past 10 years (Hyslop et al., 2013). Because of a nearly immediate impact on surface water Fe
441 concentrations and the associated ecological consequences, it is important to monitor future
442 changes in Fe sources. Sources such as Asian desert dust in our changing climate may vary
443 independently of other Fe sources such as combustion aerosols.

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

455 *4.6 Fe and Th decoupling in the deep ocean*

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

462 Variability in dissolved Fe at 1-1.5 km is clearly apparent, possibly due to hydrothermal
463 inputs. Below 1.5 km depth, Fe, ^{232}Th , and ^{230}Th display relatively constant profile shapes, at
464 least during the sparse sampling dates. From 2 km depth to the bottom, dissolved Fe is nearly
465 constant or slightly decreases with depth to about 0.5 nmol/kg, while dissolved ^{232}Th actually
466 increases with depth from 50 to 180 fmol/kg below 3000 m. This divergence in profile shape
467 already suggests a decoupling of the behavior of these elements in the deep ocean.

468 The deep ocean appears to contain an additional source for ^{232}Th . This source is
469 potentially related to resuspension of diagenetically-altered sediments at the seafloor (Hayes et
470 al., 2013a; Okubo et al., 2012). The bottom-increase in ^{232}Th begins nearly 2 km above the
471 seafloor, much higher than typical benthic vertical mixed layers (50-100 m) (Richards, 1990). This
472 phenomenon, as observed with km-scale nepheloid layers (McCave, 1986), suggests that the
473 ^{232}Th at abyssal depths of station ALOHA is being mixed in laterally from locations where
474 isopycnals impinge on surrounding bathymetry.

475 Also related to bottom sediment resuspension, the July 2012 profile of ^{230}Th displays a
476 negative concentration anomaly, or deficit of ^{230}Th , with respect to the linear profile near the
477 seafloor (Fig. 8C). This bottom ^{230}Th deficit is indicative of enhanced bottom scavenging as
478 observed in many parts of the deep North Pacific (Hayes et al., 2013b; Okubo et al., 2012). It is
479 non-intuitive that in a bottom layer where the scavenging removal of Th is enhanced compared
480 to the overlaying water column, that this layer would also be a strong source of ^{232}Th . The
481 resuspension of bottom sediments may produce such a strong release of ^{232}Th that this source
482 more than compensates for enhanced scavenging.

483 Dissolved Fe, on the other hand, appears unaffected by bottom processes, displaying only
484 a slight decrease in concentration with depth (Fig. 8A). The slight decrease with depth may be

485 related to scavenging of Fe as deep water masses age (Bruland et al., 1994). If we extend our
486 integrated residence time approach to the deep Fe profile at station ALOHA (Fig. 9), we derive a
487 whole ocean residence for dissolved Fe of only 30 years. This is significantly shorter than the
488 100-300 year estimates of the ocean residence time for dissolved Fe based on deepwater
489 scavenging (Bergquist and Boyle, 2006; Bruland et al., 1994). This discrepancy arises most
490 likely because the deep ocean source of ^{232}Th does not add dissolved Fe to the water column at a
491 crustal ratio, unlike what occurs during dust dissolution. Thus, the ^{232}Th flux method for Fe
492 residence times cannot be extended to the deep ocean.

493 The question remains: how is an element like Th, a trace component of continental
494 material, added to the deep ocean without a simultaneous release of a major crustal element like
495 Fe? The answer is likely related to solubility.

496 Dissolved Fe in the deep central North Pacific at ~ 0.5 nmol/kg has been found to be at
497 near solubility equilibrium with Fe(III) hydroxide (Kitayama et al., 2009; Kuma et al., 2003).
498 These studies determine Fe(III) solubility by adding gamma-emitter $^{59}\text{Fe(III)}$ to filtered seawater,
499 allowing the solutions to come to solubility equilibrium with Fe(III) hydroxide over several
500 weeks, subsequently filtering the seawater and then counting the ^{59}Fe gamma-activity on the
501 final filtrate. The observed ~ 0.5 nmol/kg solubility is elevated over Fe solubility in inorganic
502 seawater because of the presence of organic ligands (Liu and Millero, 2002). Thus, since the
503 deep Pacific is in a near saturation state, dissolved Fe can no longer be expected to increase, even
504 in the presence of increasing Th concentrations.

505 A problem with this argument is that electrochemically-determined Fe ligand
506 concentrations at station ALOHA are up to 2 nmol/kg, well in excess of dissolved Fe
507 concentrations (Rue and Bruland, 1995), as found in most of the world ocean (Gledhill and

508 Buck, 2012). However, it may not be appropriate to compare Fe ligand determinations directly
509 with seawater solubility. In either estimation, deepwater dissolved Fe is at least close to (within
510 the same order of magnitude) our best estimates of Fe solubility.

511 While much less is known about Th solubility in seawater, our large underestimate of Fe
512 residence time in the deep ocean implies that the deep North Pacific, with Th at ~180 fmol/kg, is
513 not near Th solubility equilibrium. Near seawater pH and ionic strength, the solubility of Th(IV)
514 hydroxide may be as high as 0.5-1 nmol/kg, compared to 1 fmol/kg for crystalline ThO₂, due to
515 the amorphous nature of Th(OH)₄ solids (Neck et al., 2003). Despite our findings of low
516 colloidal Th content, electrochemical methods suggest organic Th ligands may also exist at
517 nanomolar concentrations (Hirose, 2004). Significant organic Th could of course be present at
518 station ALOHA if the complexes are smaller than ~10 nm. We advocate direct measurements of
519 Th solubility in seawater, perhaps using radio-tracer additions with similar protocols as
520 developed for Fe (Kuma et al., 1996; Schlosser and Croot, 2008), to confirm that Th exists in the
521 deep ocean at much less than its equilibrium solubility. This would explain the fact that
522 dissolved Th concentrations continue to grow from lithogenic sources in the deep North Pacific,
523 where Fe concentrations become fixed by a solubility limit.

524 **5. Conclusions**

525 Using time-series data from the North Pacific, this study finds variability in surface Fe
526 and ²³²Th concentrations consistent with a source from Asian dust. The dust source likely has a
527 relative Fe/Th fractional solubility close to 1. The application of ²³⁰Th scavenging rates to ²³²Th
528 inventories allows the accurate prediction of the flux of dissolved metals from dust in the remote
529 surface ocean. The source flux of dissolved Fe, derived from ²³⁰Th-based timescales, suggests
530 that dissolved Fe in the upper 250 m is turning over in 1 year or less. A compelling implication

531 of this result is that Fe delivery to phytoplankton can be expected to vary with seasonal-to-
532 interannual changes in dust delivery from Asia. Continued monitoring of Fe-dependent
533 biological processes, such as nitrogen fixation, are crucial to anticipate the consequences of
534 changing land-use and/or industrial processes that may significantly affect eolian sources of Fe
535 to the North Pacific. In addition, we hypothesize that iron reaches a solubility limit in the deep
536 sea (>2 km) while Th does not, and the influx of Th cannot be used as a proxy for Fe sources in
537 this environment. Thus, the kinetic box model approach to tracing dust-derived elements (Fig. 1)
538 appears applicable only in the upper water column (~250 m).

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547

548 **Figure Captions**

549 **Figure 1.** Tracing the Fe cycle with the behavior of the long-lived thorium isotopes. Thorium-
550 230 has a well-known source from the radioactive decay of its parent ^{234}U . This allows a
551 quantitative estimate of Th removal due to scavenging on to particles. This removal rate can be
552 used to estimate the steady-state source of ^{232}Th from the partial dissolution of aerosol dust.
553 While Fe has many more terms in its biogeochemical cycling, its ultimate source from dust
554 dissolution can be predicted using known ^{232}Th fluxes and the relative solubility of Fe and Th.
555 Assuming Fe is derived only from dust, one can then estimate a maximum Fe residence time or
556 minimum turnover rate.

557

558 **Figure 2.** Depth profiles from the Hawaii Ocean Time-series station ALOHA from sampling
559 campaigns in 2012-2013. In July 2012 and June 2013, profiles for dissolved ^{232}Th (A) and ^{230}Th
560 (B) were collected in two casts (shallow to 250 m and deep to 1500 m) on different days.

561 Relative uncertainty in isotope concentrations was 1-5% and thus errors bars would be close to
 562 the symbol size. The hydrographic profiles (C-F) are shown from the shallow cast only.

563
 564 **Figure 3.** Thorium residence times, or turnover rates, calculated for the upper 150 m at station
 565 ALOHA on a monthly axis combining data from 1999 to 2014. These times are calculated by
 566 comparing integrated Th inventories to integrated production by uranium decay. The ^{234}Th -based
 567 results are reported by Buesseler et al. (2009) and Benitez-Nelson et al. (2001). Note the ^{230}Th -
 568 based results from March 2014 are not based on profiles but on single samples from 25 m,
 569 assuming uniform concentrations in the upper 150 as seen in the 2012-2013 profiles (Fig. 2).

570
 571 **Figure 4.** Station ALOHA time-series data from the surface ocean (0-10 meters depth) on
 572 dissolved (filtered at 0.45 or 0.4 μm), total (unfiltered) and particulate (digested 0.4 μm filter)
 573 ^{232}Th in full time-series (1994-2014) (A), monthly climatology (1991-2014) (B) and during a
 574 daily resolution period in July-Sept. 2012 (C). Note change in scale of y-axes at 160 fmol/kg.
 575 Results from 1994 were reported by Roy-Barman et al. (1996). Open circles represent samples
 576 collected using a mooring rather than ship-based sampling (Sec. 4.1). Relative uncertainty in
 577 dissolved, total and particulate ^{232}Th concentrations was 1-10%.

578
 579 **Figure 5.** Station ALOHA time-series data from the surface ocean (0-10 meters depth) (A),
 580 monthly climatology (B) and a daily resolution period in July-Sept. 2012 (C) of the dissolved
 581 (filtered at 0.45 or 0.4 μm), total (unfiltered) and particulate (digested 0.4 μm filter) $\text{Fe}/^{232}\text{Th}$
 582 ratio. Note change in scale of y-axes at 25,000 mol/mol. The dotted lines represent the $\text{Fe}/^{232}\text{Th}$
 583 ratio of Asian dust of $10,800 \pm 1,200$ mol/mol (1σ). Note in (C), four samples with particulate
 584 $\text{Fe}/^{232}\text{Th}$ ratios greater than 40,000 are not shown. Open circles represent samples collected using
 585 a mooring rather than ship-based sampling (Sec. 4.1).

586
 587 **Figure 6.** Depth profiles of the percentage of dissolved metals (<0.45 μm for Th or <0.4 μm for
 588 Fe) that are in the colloidal size fraction (roughly 10-400 nm) from station ALOHA in late
 589 September 2013. Colloidal content is estimated by subtracting the metal concentration in 0.4 μm
 590 filtered seawater (dissolved) from that passing through a 10 kDa membrane filter by cross-flow
 591 filtration (soluble). Colloidal fractions of ^{232}Th and ^{230}Th agree within uncertainties, while Fe
 592 colloidal content is 2-3 times larger.

593
 594 **Figure 7.** Application of dissolved ^{232}Th fluxes to predict the residence time of dissolved Fe in
 595 seawater at station ALOHA during 2012-2013. Dissolved Th residence times (A) are calculated
 596 as a function of integration depth using radioactive disequilibrium between ^{234}U and ^{230}Th . The
 597 integrated ^{232}Th inventories divided by these residence times produces an estimate of the
 598 dissolved ^{232}Th flux (B) due to dust dissolution. Assuming equal fractional solubilities
 599 dissolution and a near crustal composition for Asian dust, the flux of dissolved Fe from dust can
 600 be predicted using the second x-axis in (B). The integration of dissolved Fe inventories based on
 601 concentration profiles shown in (C) (Fitzsimmons et al., submitted), produces our estimate of
 602 dissolved Fe residence time in (D, note change in scale of x-axis at 1.2 yrs).

603
 604 **Figure 8.** Full ocean depth profiles from station ALOHA for dissolved Fe (A), ^{232}Th (B) and
 605 ^{230}Th (C) using data from this study (July 2012) and compiled from the literature. Iron data from

606 April 2001 and July 2002 were reported by Boyle et al. (2005) and from June 2002 by Morton
 607 (2010). Dissolved Th data from 1994 were reported by Roy-Barman et al. (1996). Note in (C) the
 608 dotted grey line is the linear regression of ^{230}Th data between 1 and 3.5 km, which when
 609 extended to the seafloor demonstrates that the bottom two samples are less than expected from
 610 reversible scavenging and imply enhanced scavenging (assuming no other processes affect
 611 supply and removal of ^{230}Th here).

612
 613 **Figure 9.** Application of dissolved ^{232}Th fluxes to predict Fe residence times for the full depth
 614 ocean at station ALOHA. Here data from July 2012 are used to calculate ^{232}Th fluxes (A). The
 615 depth profiles of Fe concentrations presented in Fig. 8 were averaged to calculate the dissolved
 616 Fe residence times as a function of integration depth (B). The 30 year ocean residence for
 617 dissolved Fe is significantly lower than the century-scale residence times derived by other
 618 approaches, suggesting that ^{232}Th flux may not be an accurate proxy for Fe sources in the deep
 619 ocean.

620

621 References

622

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Figure 1

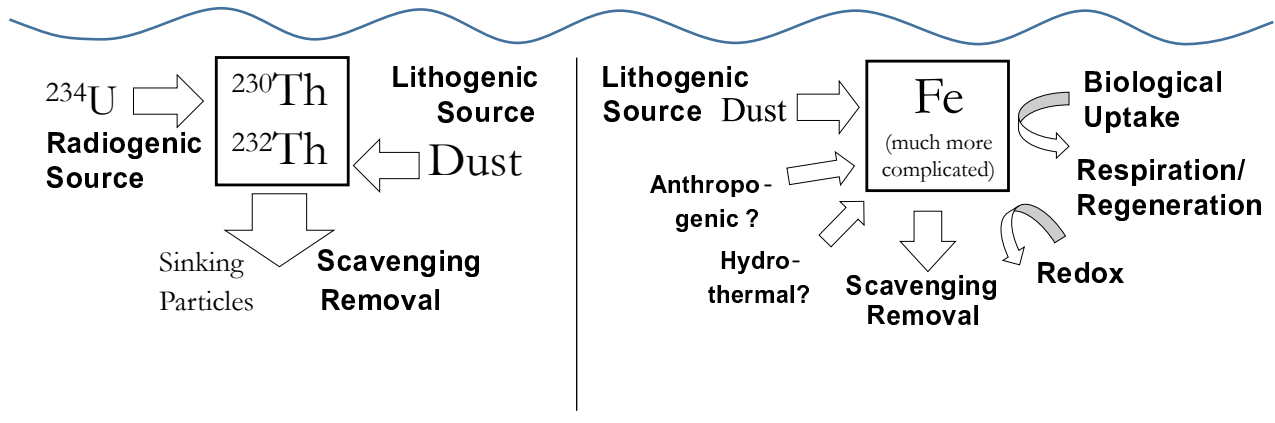


Figure 2

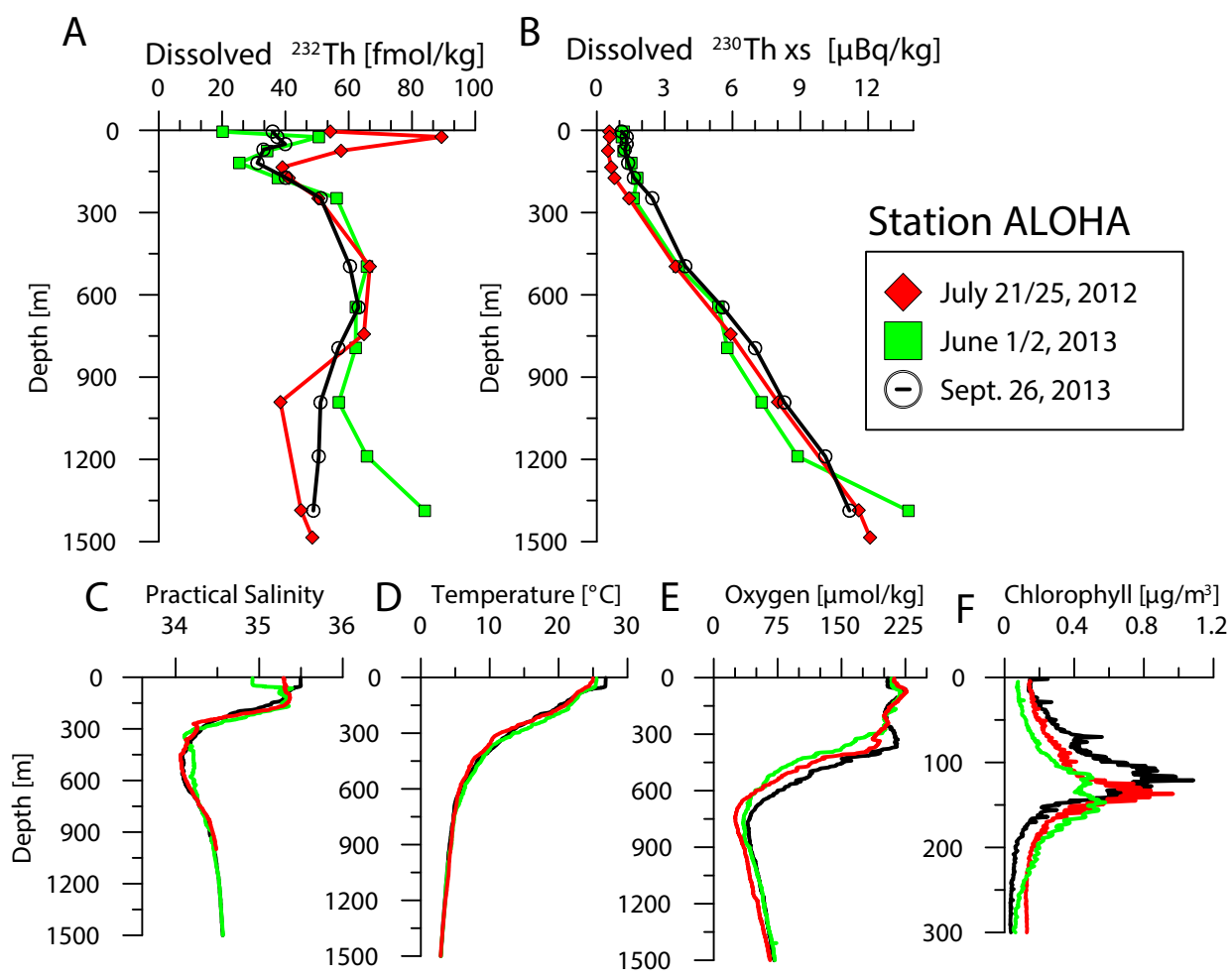


Figure 3

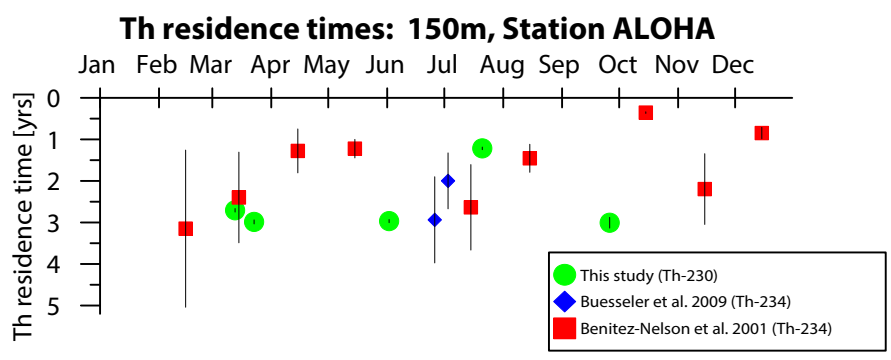


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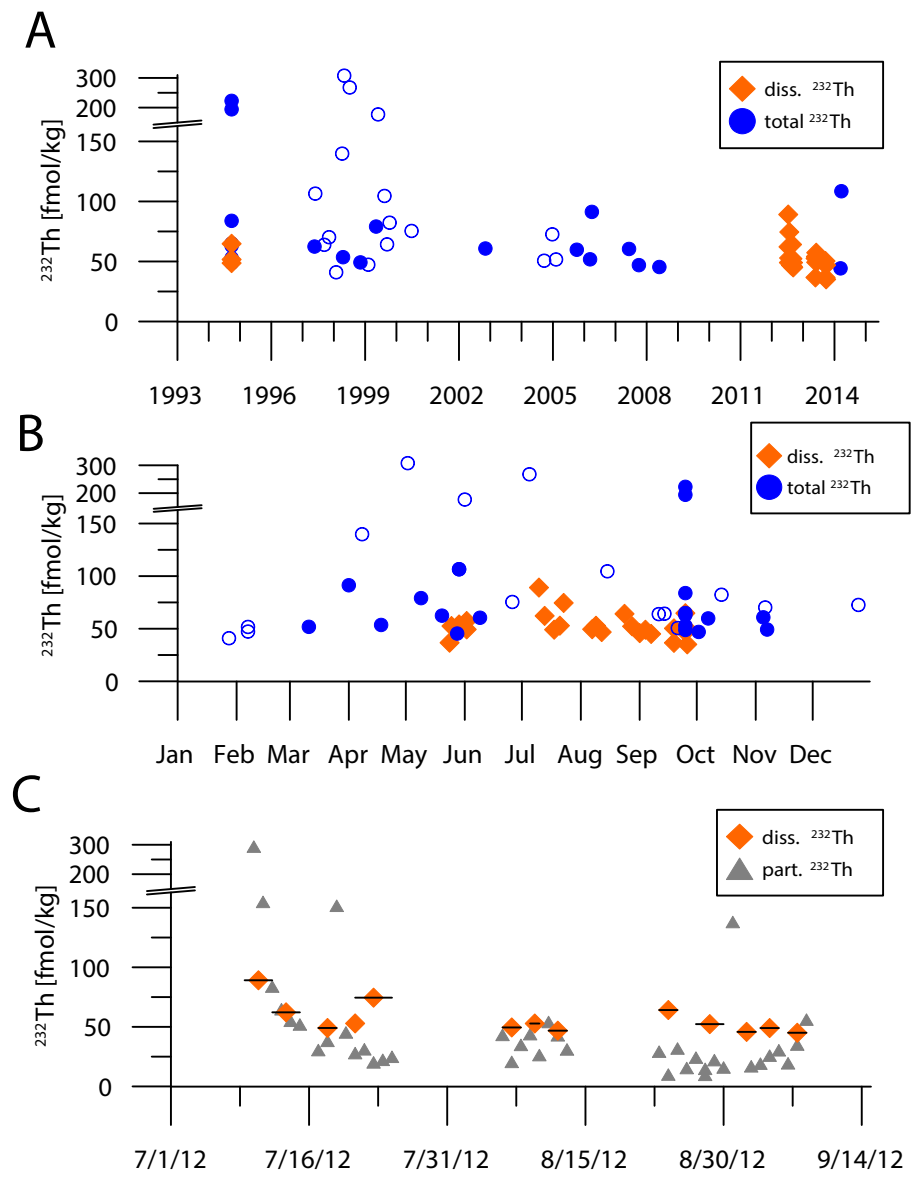


Figure 5

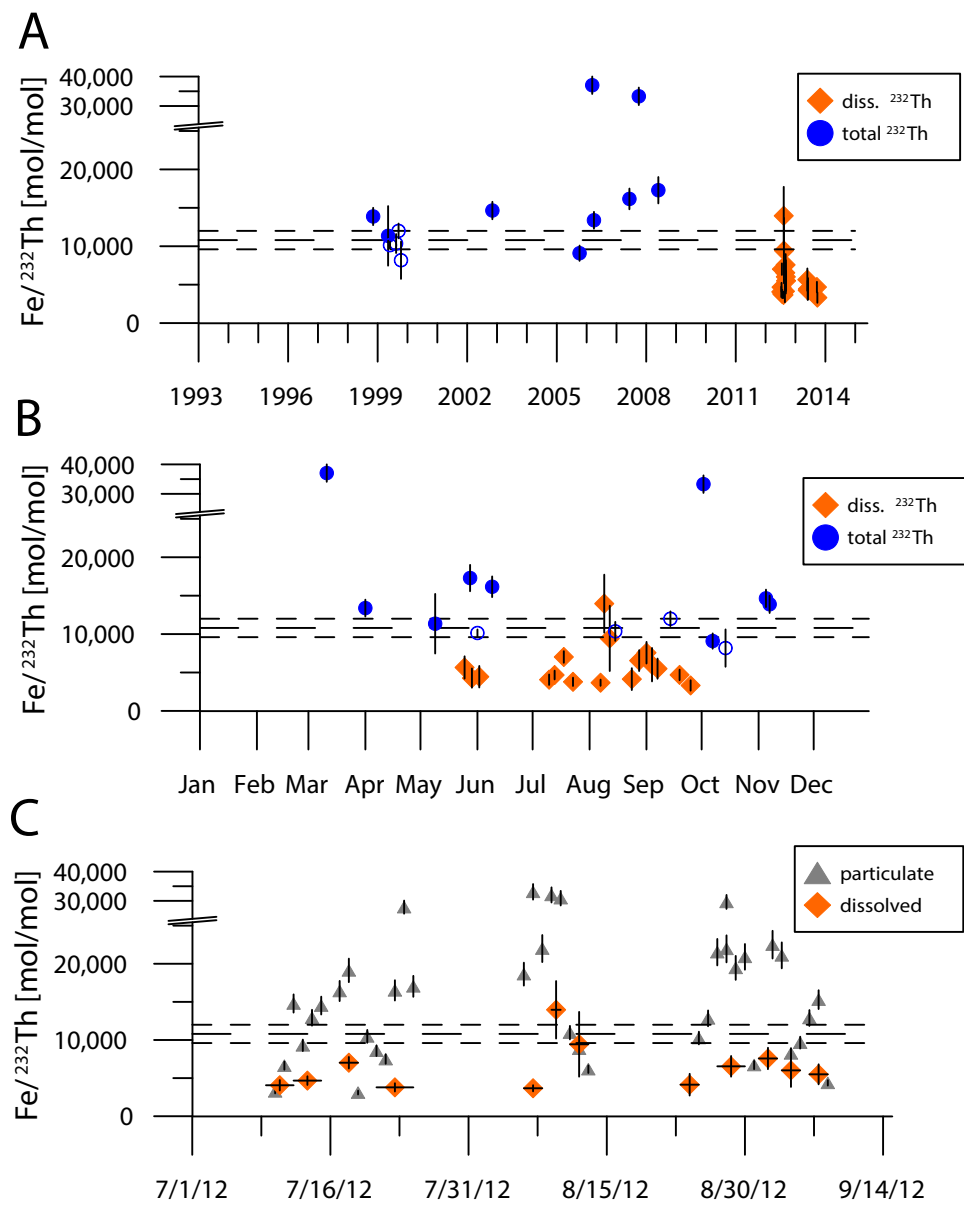


Figure 6

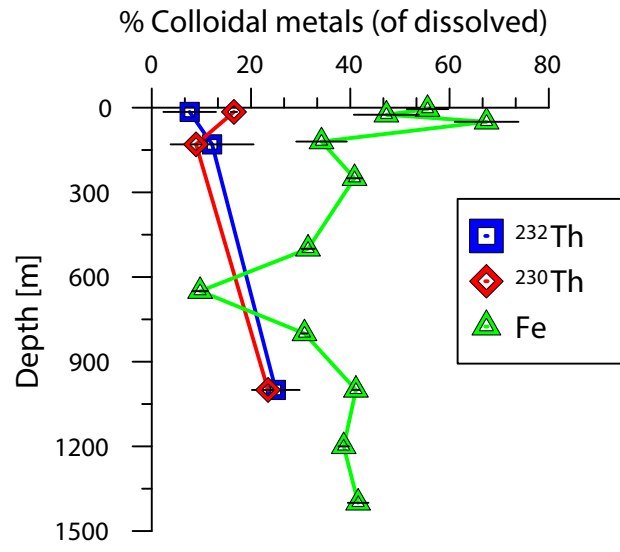


Figure 7

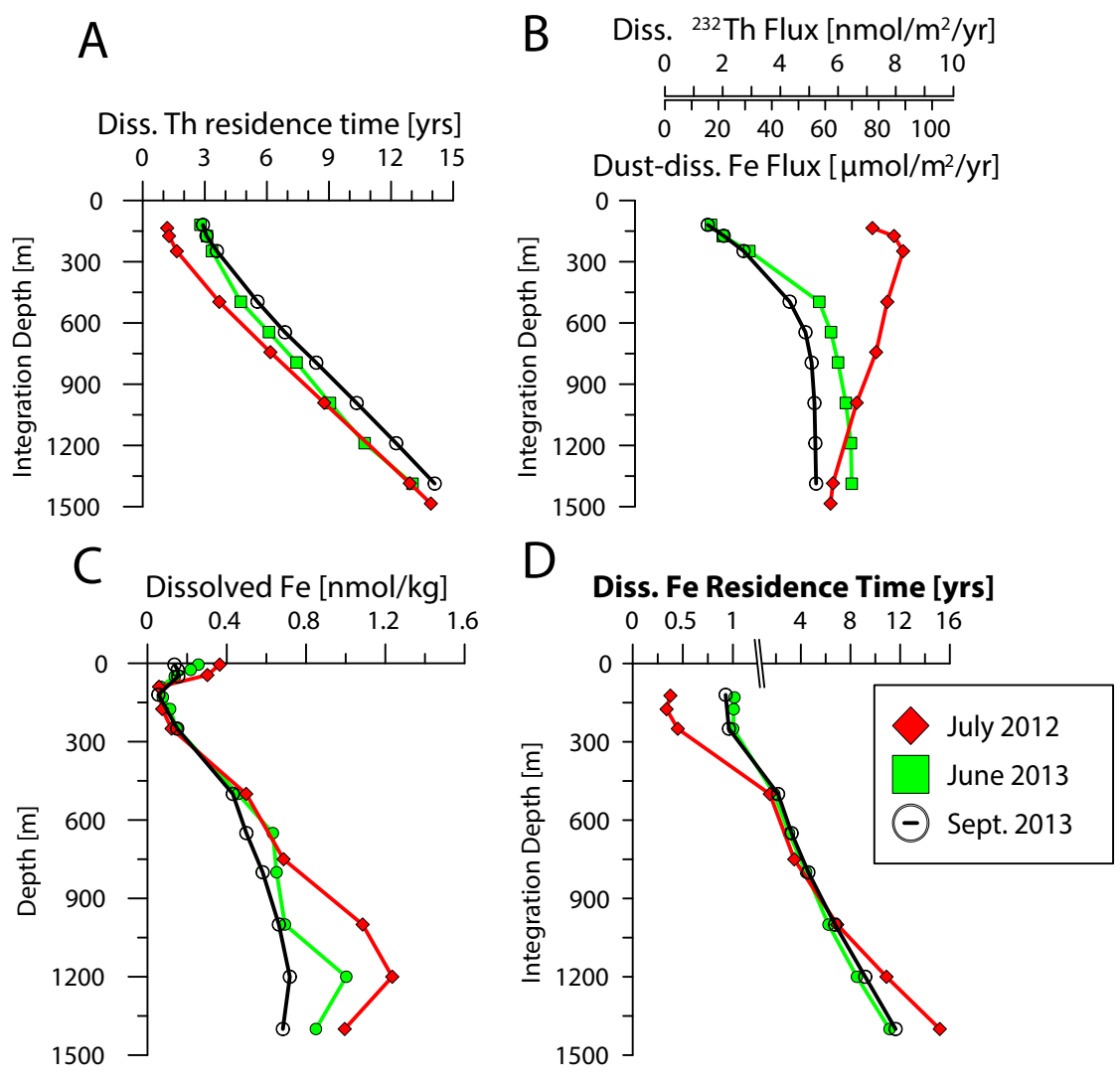


Figure 8

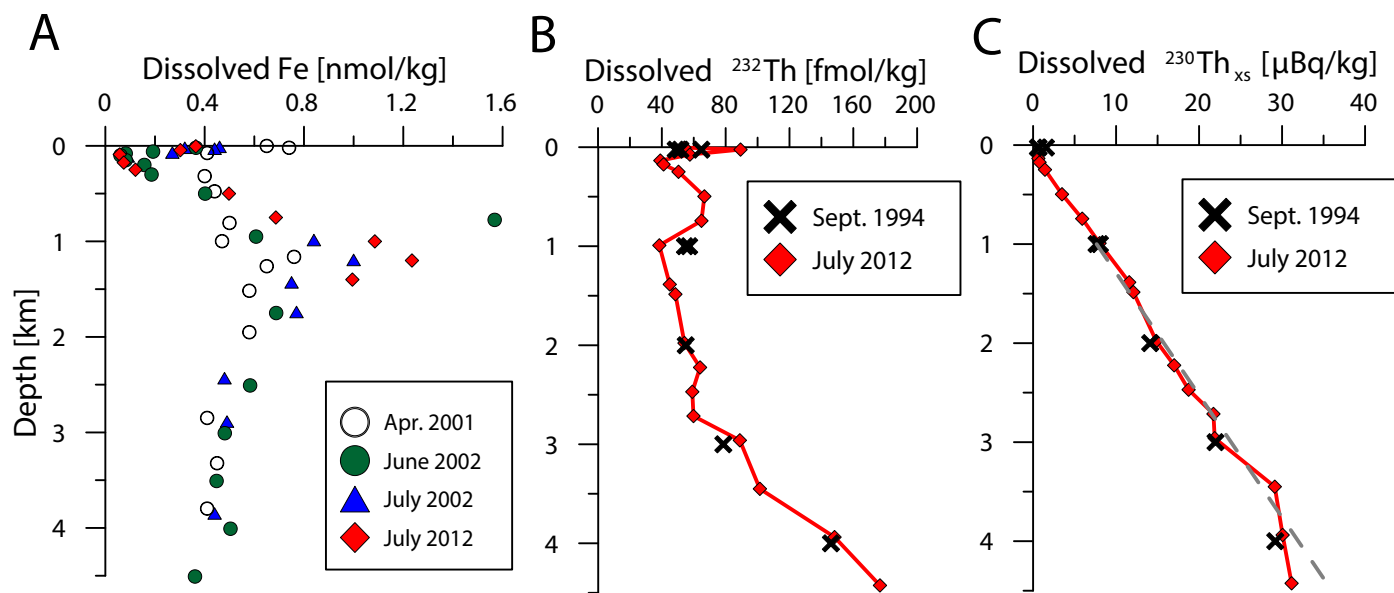
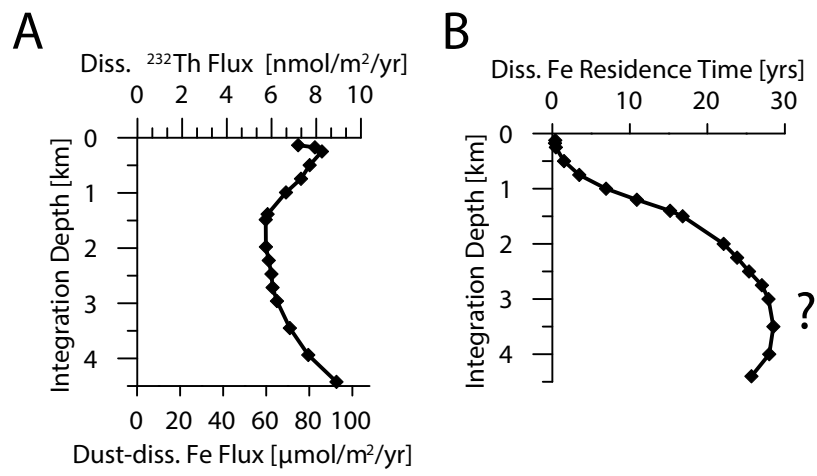


Figure 9



Electronic Annex

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