

Replacement times of a spectrum of elements in the North Atlantic based on thorium supply

Christopher T. Hayes¹, Robert F. Anderson^{2,3}, H. Cheng^{4,5}, Tim M. Conway⁶, R. Lawrence Edwards⁵, M. Q. Fleisher², Peng Ho¹, Kuo-Fang Huang⁷, Seth G. John⁸, William M. Landing⁹, Susan H. Little¹⁰, Yanbin Lu¹¹, Peter L. Morton⁹, S. Bradley Moran¹², Laura F. Robinson¹³, Rachel U. Shelley⁹, Alan M. Shiller¹, Xin-Yuan Zheng¹⁴

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¹ School of Ocean Science and Technology, University of Southern Mississippi, Stennis Space Center, MS, USA
(Christopher.t.hayes@usm.edu)

² Lamont-Doherty Earth Observatory and Palisades, Columbia University, Palisades, NY, USA

³ Department of Earth and Environmental Sciences, Columbia University, New York, NY, USA

⁴ Institute of Global Environmental Change, Xi'an Jiaotong University, Xi'an, China

⁵ Department of Earth Sciences, University of Minnesota, Minneapolis, MN, USA

⁶ College of Marine Science, University of South Florida, St. Petersburg, FL, USA

⁷ Institute of Earth Sciences, Academia Sinica, Taipei, Taiwan

⁸ Department of Earth Sciences, University of Southern California, Los Angeles, CA, USA

⁹ Department of Earth, Ocean and Atmospheric Science, Florida State University, Tallahassee, FL, USA

¹⁰ Department of Earth Science and Engineering, Royal School of Mines, Imperial College London, London, UK

¹¹ Earth Observatory of Singapore, Singapore, Republic of Singapore

¹² College of Fisheries and Ocean Sciences, University of Alaska, Fairbanks, Alaska, USA

¹³ Department of Earth Sciences, University of Bristol, Bristol, UK

¹⁴ Department of Geoscience, University of Wisconsin, Madison, Wisconsin, USA

Supplementary Text

This file contains additional results of the replacement time calculations based on dissolved ^{232}Th flux for which space in the main text did not allow discussion. In Figure S1, we show how replacement time estimates were averaged to derive a basin-wide North Atlantic average. In Figure S2, the same replacement time estimates as plotted in Figure 7 of the main text (North Atlantic basin-wide averages), but zoomed in on the upper 1000 m, to examine the replacement time results in the environment of significant biological uptake. The shortest replacement time in the upper 100 m of the bioactive elements considered is Fe, about 1–2 months. This is roughly 5 times shorter than the same estimate made at the Hawaii Ocean Time series station (Hayes et al., 2015) in the North Pacific. This implies either: (1) very rapid biological removal since the input of Fe to the North Atlantic is much greater than in the North Pacific (Hayes et al., 2017) or (2) more efficient biological retention of Fe in the Fe-poor North Pacific (Rafter et al., 2017). Zinc, cobalt, and manganese all have dissolved replacement times less than 6 years in the upper 100 m, also indicating quite rapid turnover. The derived residence time of cobalt in the upper 250 m (~5–10 years) is quite similar to that estimated in a global biogeochemical model of 7 years (Tagliabue et al., 2018). Dissolved Al has a replacement time of about 2.3 ± 0.5 years in the upper 100 m, shorter than with the usual assumption of a 5 years residence time in the mixed layer (Measures and Brown, 1996). Copper and cadmium have much longer replacement times in the upper 100 m (80–90 years), perhaps surprisingly given their role as micronutrients. Of course, as discussed in the main text, there are large uncertainties with respect to source composition and relative solubility especially for these elements.

In figures S3 and S4, we show replacement time calculations for other elements of geochemical interest, for which data are available in the GAO₃ data product: Sc, V, Ni, Ga, and Ba. Sections plots are shown in Figure S3 and the North Atlantic averages in Figure S4. For these estimates we have used the assumption of upper continental crustal source (Rudnick and Gao, 2014) and any available data from the DI leaches (Shelley et al., 2018) (see Table S1). Based on enrichment factor analyses, North African dust is contaminated with anthropogenic V and Ni (Shelley et al., 2015; Trapp et al., 2010). This potentially leads the V/Th and Ni/Th solubility ratios (reported in Table S1) being elevated over natural inputs and thus may lead to our replacement time estimates for V and Ni being underestimates of the residence time. Available leach data for Sc and Ga was minimal, so we made a basic assumption of similar fractional solubility to Th for Sc ($S_{\text{Sc}}/S_{\text{Th}} = 1$) since this is a highly scavenged element (Parker et al., 2016) and greater solubility for Ga than Th ($S_{\text{Ga}}/S_{\text{Th}} = 5$) since this element is scavenged less intensely than Al (Shiller and Bairamadgi, 2006) and thus likely much less intensely than Th. Deep ocean estimates indicate Sc and Ga are relatively short-lived, with 5 km replacement times of about 160 years or less, and both elements may be good analogues for lithogenic, scavenged elements like thorium. Barium and nickel have intermediate length replacement times (5 km replacement times of about 5,000 years), which indicates their role in biological cycles. Consistent with the Th-based result, whole ocean Ba replacement time is estimated as about 10,000 years (Chan et al., 1976). The deep ocean replacement time of dissolved vanadium is about 15,000 years, much longer than deep ocean mixing timescales, indicative of its role as a quasi-conservative oxyanion species.

In the upper 100 m, Sc and Ga replacement times are relatively short, roughly 10 years for both elements. Till et al. [2017] recently independently assessed the upper water column residence time of Sc as 5.6 ± 3.2 years near Bermuda, grossly consistent with the Th-based one, or perhaps suggesting the Sc/Th relative solubility may be somewhat greater than 1, which would have reduced the Th-based estimate. The Ga replacement time is roughly consistent with the decadal-scale residence time inferred for this element in the North Atlantic (Shiller, 1998). The surface ocean Ba residence time of ~200 years is longer than the ~25 years estimated by Lea and Boyle [1991]. We are not aware of a good basis for comparison for the surface water replacement time estimates of V or Ni.

Finally, in Figure S5, we show the deep ocean residence time results based on the replacement time estimates for all elements considered in this study in the form of a periodic table, with comparison to available residence time estimates for most other elements in the periodic table. Note, as discussed in the main text, replacement times are not necessarily equivalent to residence times, but we make that assumption here in order to see the overall pattern observed among the elements. A broad scale feature is apparent of long residence times for the left and right sides of the table (alkalis, alkali earths, and halogens) with short or intermediate residence times for the nonmetals, transition metals and lanthanides. Within the transition metals, there are interesting non-monotonic trends that, upon a more detailed analysis than attempted here, may provide further insights in the cycling of elements in the ocean.

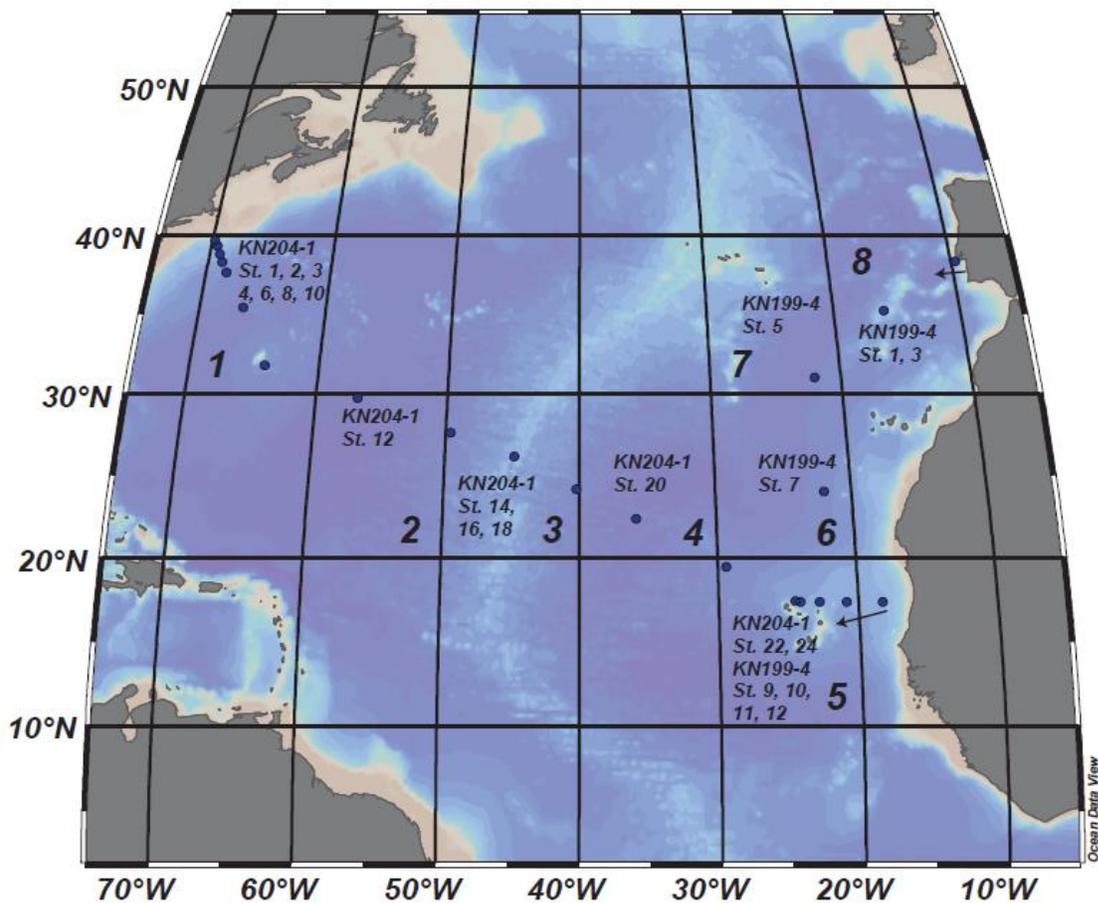


Figure S1. Location of GA₀₃ stations for which replacement time estimates of trace elements can be made based on measured ²³²Th supply. GA₀₃ consisted of two cruises (KN199-4 from Portugal to Cape Verde and KN204-1 from Cape Cod to Cape Verde). To make a North Atlantic basin residence time estimate, the replacement time profiles at these stations were first binned into a common depth scheme. Depth bins were 0-100 m, 100-500 m, 500-1000 m, 1000-1500 m, 1500-2100 m, 2100-3000 m, 3000-4000 m, 4000-5000 m and 5000-5500 m, and were chosen to have at least one observation of ²³²Th in each bin at each station. The station profiles within the 10° x 10° boxes labelled with a large number in the map (1 thru 8) were then averaged across depth bins. The averaged profiles from each numbered box were subsequently averaged with an area-weighting factor, taking into account the

relative area of the different boxes. KN199-4 Station 1 on the Portuguese coast was averaged in Box 8 and KN199-4 St. 9 on the Mauritanian coast was averaged in Box 5.

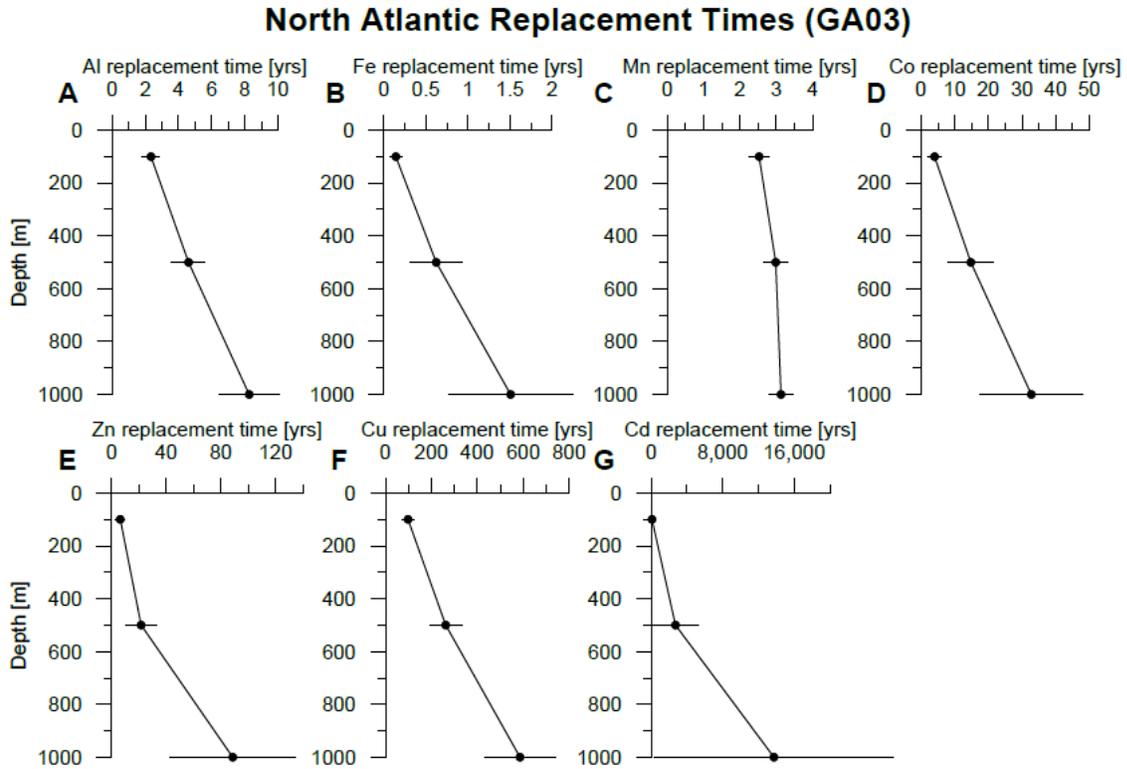


Figure S2. Residence time estimates in the upper 1000 m for dissolved elements with respect to dissolved ^{232}Th supply averaged for the North Atlantic basin using GA03 stations. The error bars represent the standard deviation of estimates arising from using either upper continental crustal or North African dust metal/thorium ratios and metal/thorium fractional solubility ratios defined by HAc or DI leaches of North African dust (Berger et al., 2008; Shelley et al., 2018).

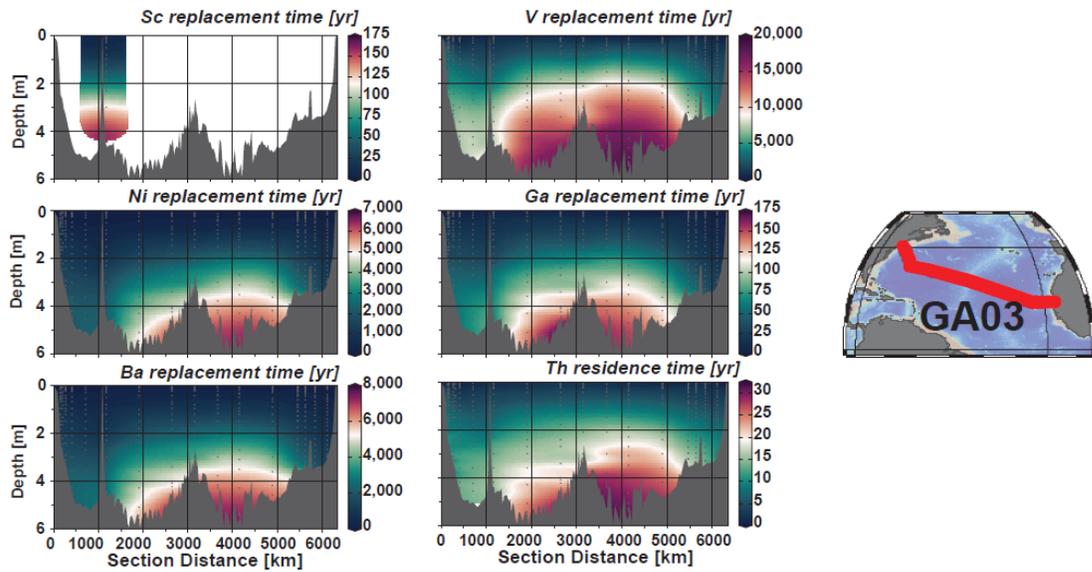


Figure S3. Replacement time estimates across the GA03 section for dissolved Sc, V, Ni, Ga, Ba and Th, with respect to dissolved ^{232}Th supply, upper continental crustal metal/thorium ratios (Rudnick and Gao, 2014) and metal/thorium fractional solubility ratios defined by deionized water leaches of North African dust (Table S1; Shelley et al., 2018). Dissolved Sc data were only available from 1 stations from GA03 (KN204-1 St. 10, co-located with BATS) (Parker et al., 2016). Data on dissolved V, Ni, Ga and Ba are published here for the first time, <https://www.bco-dmo.org/dataset/3827>. Th residence time is based on ^{230}Th scavenging which is considered in steady-state with supply by ^{234}U decay.

North Atlantic Replacement Times (GA03)

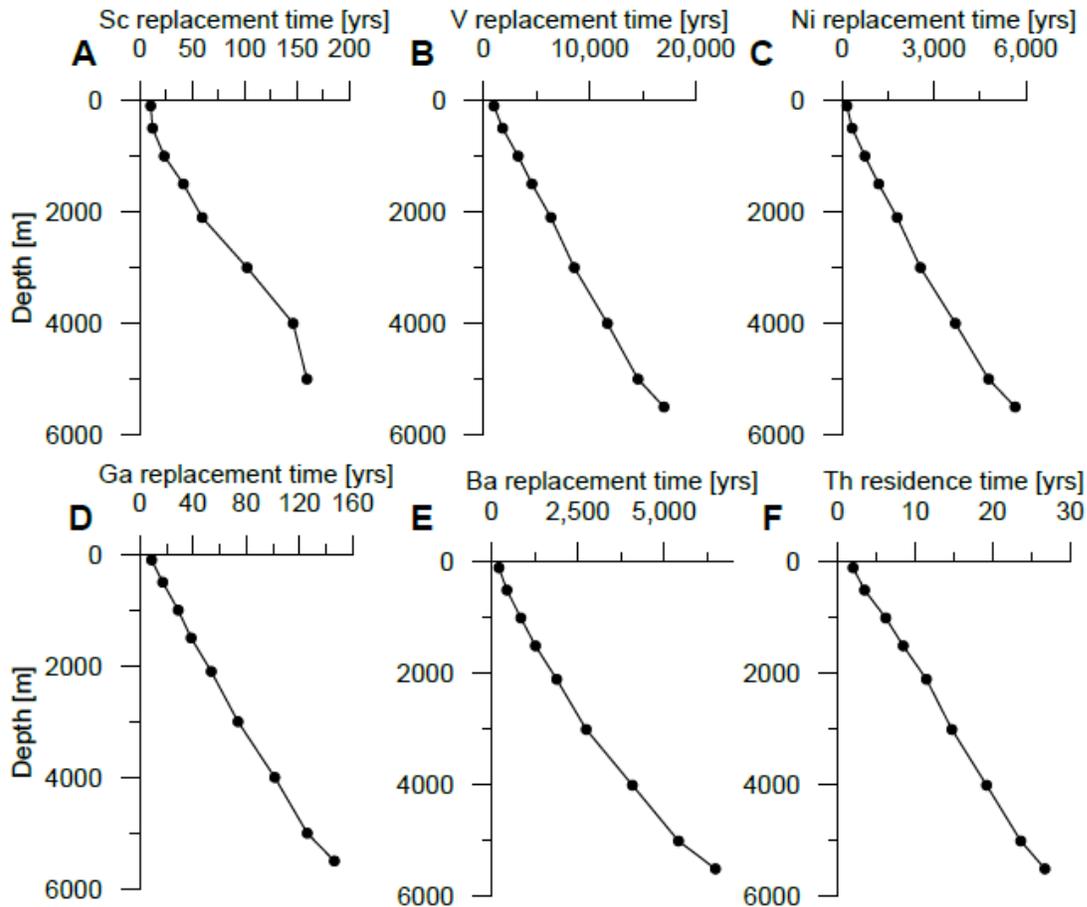


Figure S4. North Atlantic replacement time estimates for dissolved Sc, V, Ni, Ga and Ba, with respect to dissolved ^{232}Th supply, upper continental crustal metal/thorium ratios (Rudnick and Gao, 2014) and metal/thorium fractional solubility ratios defined by deionized water leaches of North African dust (Table S1; Shelley et al., 2018), or assumed (see Table 2). Dissolved Sc data were only available from 1 stations from GA03 (KN204-1 St. 10, co-located with BATS) (Parker et al., 2016); therefore, this profile is not a basin average but is likely representative of the subtropical gyre. Dissolved V, Ni, Ga and Ba data are published here for the first time (personal communication). Th residence time is based on ^{230}Th scavenging which is considered in steady-state with supply by ^{234}U decay.

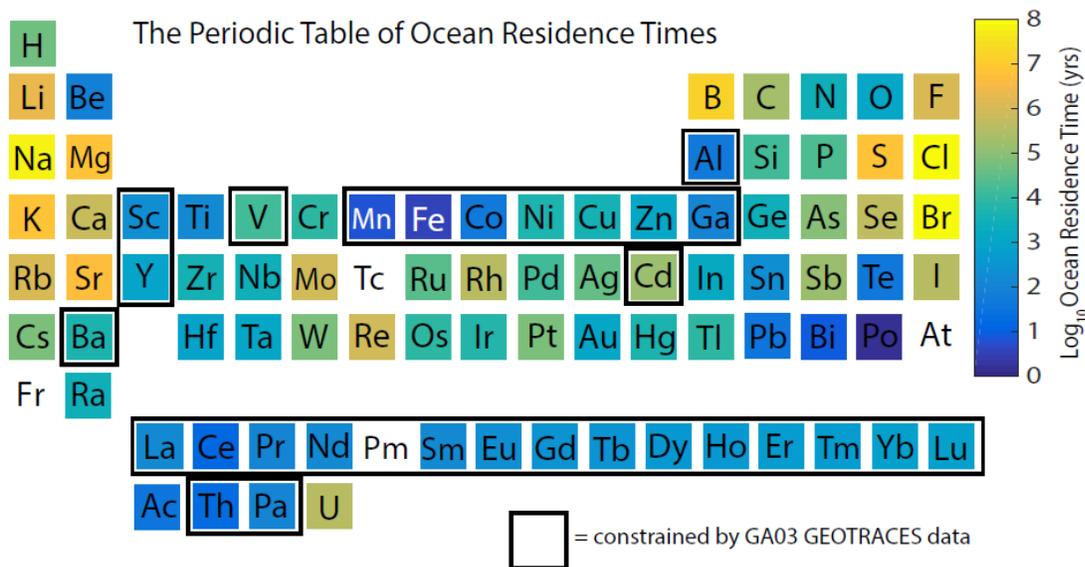


Figure S5. Residence times of the elements in the ocean, or the average time an element spends in the ocean between its supply and removal. New residence time estimates (outlined in black boxes) are based on the replacement times calculated in this study which were derived by comparing measurements of the element's dissolved inventory to its supply based on measured dissolved ^{232}Th supply integrated for the whole North Atlantic covered by GEOTRACES section GA03 (see main text for data citations), assuming an upper continental crustal (UCC) composition (Rudnick and Gao, 2014) of the material that supplies the elements and an informed estimate of the elemental solubility of UCC material based on deionized water leaches of North African dust aerosol samples (Shelley et al., 2018). The following references were used for the residence times of the other elements: H (as H_2O) (Berner and Berner, 2012); Li, B, Na, Mg, P (as dissolved inorganic phosphorous), S (as sulfate), Cl, K, and Ca: (Chester and Jickells, 2012); Be, F, Ge, As, Se, Rb, Ru, Pd, Ag, In, Sn, Sb, Se, Te, Cs, Ir, Pt, Hg, Tl and Bi: (Li, 1991); C (as dissolved inorganic carbon), N (as nitrate) and O (as molecular oxygen): (Broecker, 2015); Si (as dissolved inorganic silicon): (Sarmiento and Gruber, 2006); Sc (Parker et al., 2016); Ti: (Orians et al., 1990); Cr: (Reinhard et al., 2013); Br, Sr and I (as iodate): (Broecker and Peng, 1982); Zr, Nb, Hf and Ta (Firdaus et al., 2011); Mo and W: (Sohrin et al., 1998); Rh: (Bertine et al., 1993); Re: (Colodner et al., 2014); Os: (Oxburgh, 2001); Au: (Falkner and Edmond, 1990); and U: (Ku et al., 1977). Note that Tc and Pm (and the trans-uranics, not shown) are not naturally-occurring in the ocean and thus residence times are not given. Residence times of Po and At (and Fr and Ra, not shown) are limited by the length of their radioactive half-lives. Pb has been contaminated in the ocean by anthropogenic input and thus a steady-state residence time is not appropriate to define. The Pb residence time given (150-100 years) is based on residence times of ^{210}Pb with respect to scavenging derived by (Bacon et al., 1976). The noble gases are essentially non-reactive in the ocean, and therefore, these elements are not shown.

Table S1. Upper continental crust compositional ratios (Rudnick and Gao, 2014) and DI leach (Shelley et al., 2018) solubility ratios used in the residence time calculations presented above. The choice of these ratios is a large source of uncertainty in this method of estimating residence time based on thorium supply. Compositional ratios and solubility ratios are likely to differ for different sources (North African dust versus rivers versus hydrothermal vents, etc.). A more complete analysis of the sensitivity of these ratios to these factors is beyond the scope of this contribution.

	Sc	V	Ni	Ga	Ba
Me/Th (UCC) [mol/mol]	6.88	42.07	17.69	5.55	101.04
S_{Me}/S_{Th} (DI leach, or assumed; see supplementary text)	1 (assumed)	25 ± 19 (n = 12)	29 ± 25 (n = 12)	5 (assumed)	12 ± 5 (n = 12)

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