PERSPECTIVE

TIMEKEEPERS FOR TRACE ELEMENTS IN THE GLOBAL OCEAN
THE THORIUM STOPWATCHES

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ABSTRACT. The various isotopes of thorium offer oceanographers tools for tracking particulate matter in the ocean across multiple timescales. To learn about the cycling of trace elements in the ocean, in this perspective we focus on the latest applications of thorium's longest-lived naturally occurring isotopes: ^{232}Th, ^{230}Th, ^{228}Th, and ^{234}Th. From desert dust to marine snow to sediment porewaters, thorium measurements can be used to derive rates of trace element input and removal, using the assumptions of radioactive disequilibrium. Opportunities exist to fine tune and improve the application of these already versatile stopwatches, but GEOTRACES-era data clearly demonstrate their utility.

INTRODUCTION

The element thorium is very insoluble in the ocean, a property shared by many other trace elements (Goldberg, 1954). This characteristic makes thorium useful as a tracer (Krishnaswami et al., 1976). The upper continental crust is already low in thorium—there are about 10 micrograms of thorium per gram of crust (Rudnick and Gao, 2014). In seawater, its abundance is even smaller—the average dissolved thorium concentration in the ocean is ~0.1 picomolar, or 0.4 femtograms (0.4×10^{-15} g) Th per gram of seawater (Schlitzer et al., 2018). In other words, thorium is 25 billion times more concentrated in the crust compared to seawater. The little thorium that does make it into the dissolved phase in seawater (operationally defined as that which passes through a filter of ~0.45 μm) comes from partial dissolution of crustal material or from the radioactive decay of a soluble parent isotope.

Because of its dislike of an aqueous environment (Santschi et al., 2006), dissolved thorium in the ocean will be adsorbed onto particulate material, or "scavenged," and eventually become buried in marine sediments.

The insolubility of thorium, and its well-known production from the decay of its parent isotope, are the key ingredients for making thorium a stopwatch in the ocean. Radioactive decay chains, if left undisturbed, tend toward secular equilibrium. This means that the radioactivity (in decays per second) of parent and daughter isotopes is equal. This radioactivity balance cannot always exist in seawater because as soon as thorium is injected into water, it quickly becomes attached to sinking particles and is removed from the water. On timescales of weeks to months, we can use the extent of removal of thorium compared to its parent to derive a timescale of removal. On longer timescales of years to decades, the extent of thorium removal from the dissolved phase is virtually complete. In the longer-term case, we can usually assume that all of the thorium that was introduced into the water over a given period of time will have been removed and is either traveling downward in the water column on sinking particles, or is completely removed from the water column and buried in the sediments.

TRACING PARTICLE EXPORT WITH ^{234}Th

We begin this isotopic perspective with the shortest-lived, yet heaviest by weight, of the isotopes considered here, ^{234}Th. It is the radioactive progeny of the most abundant form of uranium in seawater, ^{238}U, which is well-mixed throughout the ocean (Figure 1). ^{234}Th itself has a half-life of 24 days. The shorter an isotope's half-life, the faster that secular equilibrium with its parent is approached. The scavenging removal process needs to happen fast enough to occur before the ongoing decay of ^{238}U can resupply the ^{234}Th (Bhat et al., 1969). Deficits of seawater ^{234}Th activity compared to its production by ^{238}U decay typically occur most conspicuously in the upper 150 m of the water column (Buesseler et al., 1992; Ceballos-Romero et al., 2022), where the largest vertical sinking, or export, of particulate matter occurs, as well as near the seafloor,

where resuspension of sediments results in enhanced scavenging (Bacon and Rutgers van der Loeff, 1989).

A specific elemental removal rate is difficult to otherwise estimate in the environment and is very useful in considering an element's turnover, or residence, time. In an ecosystem, the residence time of the micronutrient iron, for instance, is a critical timescale for all the living things that require this iron for their biological functioning. Working with data from the international GEOTRACES program, Black et al. (2020) quantified the removal rate of ^{234}Th from the upper ocean throughout the North Atlantic and South Pacific using the deficit method described above. Figure 2 shows some of the North Atlantic ^{234}Th data (Owens et al., 2015), which exhibits a characteristic "deficit" of ^{234}Th in the upper ~150 m, the extent of which is used to estimate particle export flux from the upper water column. Black et al. (2020) make the connection to trace element cycling by taking the removal rate analysis one step further and predicting how much iron is being removed by this particle export process. These authors further constrain upper ocean iron residence times on a vast scale by comparing ^{234}Th-based Fe removal rates with the measured inventory of Fe. The majority (67%) of new estimates of the total Fe residence time in the upper 250 m of the ocean fall within 10–100 days, a shorter timescale than previously thought, in some cases an order of magnitude shorter. Note that the ^{234}Th stopwatch is well positioned to track this timescale of weeks to months as it approaches 5 times 24 days, or the timescale on which ^{234}Th would return to secular equilibrium.

TRACING BENTHIC ELEMENT SUPPLY WITH ^{228}Th (AND Ra)

Moving up in half-life, ^{228}Th offers another kind of stopwatch, with applications for both trace element removal and trace element supply from benthic sediments. This isotope is sandwiched in a decay chain between a series of radium isotopes. The parent ^{228}Ra (half-life 5.8 years) undergoes two beta decays and a short-lived intermediary to form ^{228}Th (half-life 1.9 years), which subsequently alpha decays into ^{224}Ra (half-life 3.6 days). In contrast to all Th isotopes, Ra is relatively soluble in seawater. While ^{228}Th :^{228}Ra considerations can be used to quantify particulate scavenging removal (Figure 1; Hayes et al., 2018a) similar to ^{234}Th, we focus here on a different application, using ^{228}Th as the parent isotope rather the progeny.

The ^{228}Th in sediments supplies a constant source of ^{224}Ra to sediment porewaters (Figure 1). Some of that ^{224}Ra escapes into bottom seawater through processes of sediment irrigation and advective flows, and this ^{224}Ra source is demonstrated in the North Atlantic dataset shown in Figure 2 (Charette et al., 2015). The deficit of ^{224}Ra within sediment porewaters with respect to its parent ^{228}Th can further be used to derive a flux of ^{224}Ra to bottom seawater (Cai et al., 2014). Extrapolation to benthic porewater fluxes of other elements can be accomplished using the porewater concentration gradients of those other elements. Shi et al. (2019) used this ^{224}Ra/^{228}Th method to study coastal sediments throughout eastern China to estimate benthic fluxes of iron from the sediments. Although iron is very insoluble in oxygenated seawater, in the conditions found in sedimentary porewaters, Fe can be released into the dissolved phase (likely as colloids) in great proportions through both reductive and nonreductive pathways to build up concentrations much larger than that found in seawater (Homoky et al., 2021). The Shi et al. (2019) study investigated relatively shallow sites, with water depths ranging
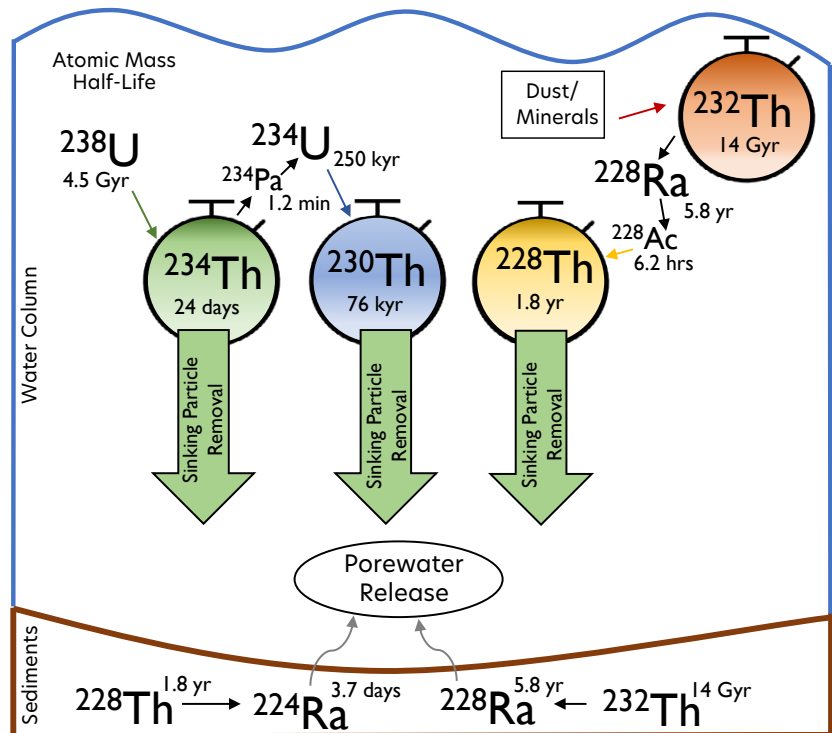

FIGURE 1. Thorium isotopes as stopwatches used for oceanographic applications. ^{232}Th is a primordial isotope with its own decay chain, including ^{228}Ra, ^{228}Th, and ^{224}Ra. ^{234}Th and ^{230}Th are radiogenic and are part of the ^{238}U decay chain. Many other trace metals are involved in the processes of sinking particulates and porewater release, for which thorium provides important timescale information. The intermediaries ^{234}Pa and ^{228}Ac are essentially ignored in these processes because they are very short-lived. Note that the decay chains extend beyond the isotopes shown here (Geibert, 2008; Rutgers van der Loeff and Geibert, 2008), ultimately into stable isotopes of lead, but these are omitted for clarity.
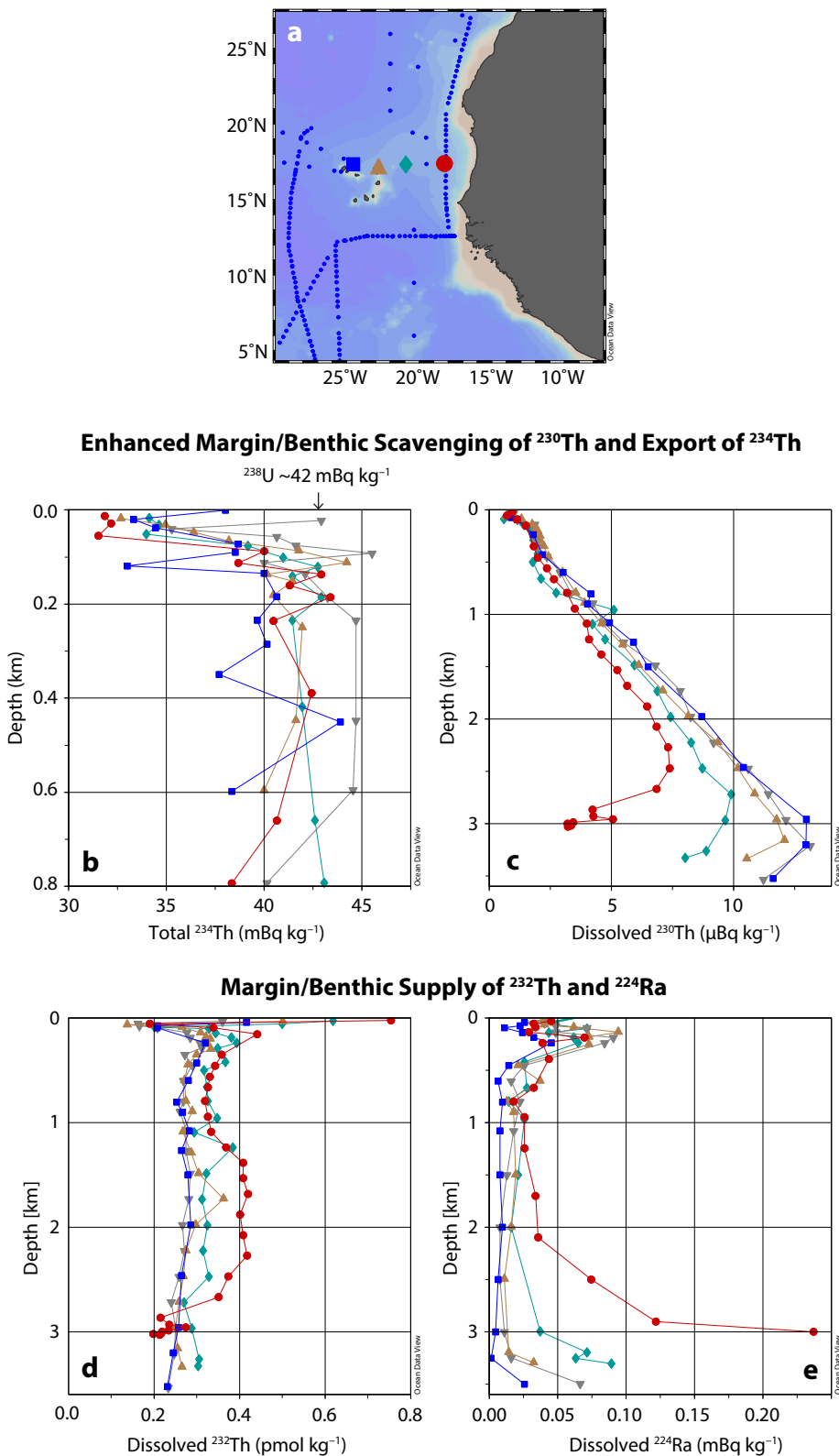
Enhanced Margin/Benthic Scavenging of ²³⁰Th and Export of ²³⁴Th

$^{238}U \sim 42$ mBq kg^{-1}

Margin/Benthic Supply of ²³²Th and ²²⁴Ra

FIGURE 2. GEOTRACES data demonstrating variations in Th isotope behavior from North Atlantic section GA03. (a) On the map of the West African margin, plotted station data are shown as colored symbols, and small blue dots indicate other available data in the GEOTRACES Intermediate Data Product. The depth profiles show (b) total (dissolved + particulate) ²³⁴Th (Owens et al., 2015) and also the uniform activity of ²³⁸U (note unique depth scale), (c) dissolved ²³⁰Th (Hayes et al., 2015), (d) dissolved ²³²Th (Hayes et al., 2018b), and (e) dissolved ²²⁴Ra (decay product of ²²⁸Th; Charette et al., 2015).

from 0 to 80 m. Within that range, they found much greater benthic iron fluxes at sites shallower than 20 m depth, a trend the authors ascribe to greater mixing and wave energy irrigating the porewaters at the shallower sites. They also found that the Fe fluxes derived from the Th method were up to orders of magnitude larger than those detected with previous methods using benthic lander chambers that can make very detailed porewater measurements at a particular landing site. It may be that the Th method is a better spatial integrator of fluxes spread out over a particular coastal area, and the benthic lander method presents a sampling bias. Much more is to be learned about benthic pore water fluxes as this method is applied to other regions. In particular, benthic fluxes of copper and aluminum have long been thought important to the overall cycling of these elements, which could also be quantified in this way. A similar method can be applied to the longer-lived ²²⁸Ra, whose parent is ²³²Th (**Figure 1**; e.g., Sanial et al., 2018), with some slightly different assumptions (Charette et al., 2016).

TRACING SCAVENGING AND PARTICLE FLUXES WITH ²³⁰Th

There is a large jump in time to the next longest-lived Th isotope, ²³⁰Th, with its half-life of 76,000 years, but it can provide information on particle sinking rates on longer timescales. Similar to ²³⁴Th, ²³⁰Th is produced in the ocean by another uniformly distributed uranium isotope, ²³⁴U (**Figure 1**). Once injected into the dissolved phase by alpha decay, ²³⁰Th does not stay in seawater for 76,000 years, because it is so insoluble that it is scavenged and buried in the sediments on the timescale of years to decades (Henderson and Anderson, 2003). Accordingly, within the water column, ²³⁰Th can record events on the timescale of its water column residence rather than on the timescale of its radioactive half-life. In the sediment, ²³⁰Th inventories can record changes in particulate matter burial up to ~400,000 years ago (Costa et al., 2020). We won't go that

far back in time here, but past ocean particle fluxes are important, for example, for understanding the ocean's uptake of carbon dioxide and global climate.

As in the case of [234]Th-derived particle fluxes of Fe, [230]Th can also be used to estimate the downward sinking flux of other particulate elements. Dissolved [230]Th in the water column is generally inversely proportional to the intensity of particle scavenging (Figure 2). However, for the particulate phase [230]Th, the assumption would be that all of the [230]Th produced by [234]U decay above a given depth horizon in the water column is settling toward the seafloor. This known flux can be used as a normalization to estimate the sinking flux of other elements (Bacon and Rosholt, 1982). Especially deeper in the water column (~2 km), [230]Th-normalized flux on water column particles is one of the only methods for estimating a sinking particulate flux, aside from the traditional technique of deep-moored sediment traps.

Rahman et al. (2022) used the particulate [230]Th technique to investigate the ocean cycle of particulate barium in GEOTRACES transects. While barium is not an essential micronutrient like some other trace metals, it may be a useful proxy for biological productivity. Barium tends to precipitate as barite (or barium sulfate) in sinking aggregates of particulate organic matter, but it is relatively well preserved as it sinks in the water column and is subsequently buried, whereas almost all of the organic matter tends to be respired before burial. By comparing sinking rates of barium in the deep water column with barium burial rates in the sediments, these authors were able to determine that preservation efficiencies of this potential proxy for organic matter export varied a great deal (between 17% and 100% across the North Atlantic and South Pacific). This study raises some important questions on the reliability of particulate barium as a proxy in the sediments and warrants further investigation into the controls on barite preservation, part of which may involve the seawater barite saturation state (Mete et al., 2023).

TRACING DUST AND BENTHIC SUPPLIES WITH [232]Th

The isotope [232]Th makes up nearly all (99.98%) of the thorium in Earth's crust on a per weight basis and can provide critical information on trace element supply from mineral sources. Mineral dissolution is one of the main suppliers of the micronutrient iron to the ocean, and its scarcity can limit biological rates in certain regions. Iron measurements alone cannot always determine its main sources, and therefore tracers of its supply are quite useful to oceanographers.

[232]Th does not come from the decay of anything but is primordial in the sense that this element was included in the star dust that coalesced to originally form our planet. Its extremely long half-life (14 billion years) means that on most timescales considered in the water column or sediments, the effect of its own radioactive decay on its concentrations can be ignored. Therefore, we don't truly use [232]Th as a stopwatch itself, but we can use the timescale information from other thorium isotopes to measure how quickly [232]Th is moving around. While potentially any of the other stopwatch isotopes could be used for this, [230]Th has been paired most often, because both of these isotopes are abundant enough to be routinely measured by mass spectrometry (i.e., counting the number of atoms in a sample). The shorter-lived [234]Th and [228]Th are still measured by counting their radioactive decay and are truly miniscule on a per atom basis.

It is worth mentioning briefly here what advances the community has made in analyzing thorium isotopes in the environment, especially for the long-lived isotopes that have the lowest activities. Some of the first precise measurements of [232]Th and [230]Th reported in seawater (Moore and Sackett, 1964) were made using ~200 liter water samples, which was roughly the necessary size sample needed to detect these isotopes using alpha decay counting. With advances in mass spectrometry in the 1980s and 1990s, the first paired mass

spectrometry measurements of [232]Th and [230]Th indicated that sample volume could be reduced to 1 liter (Roy-Barman et al., 1996). This reduction in volume needed drastically increased the sample throughput that could be achieved and ultimately made possible GEOTRACES section-type data for these isotopes (e.g., Figure 2).

As mentioned at the beginning, the main source of the dissolved phase of [232]Th in the ocean is the partial dissolution of crustal material. In the remote open ocean, the primary source of crustal material is wind-blown dust from upwind desert regions. The North Atlantic dataset in Figure 2 shows that increased [232]Th concentrations near the West African margin are likely due to both dust and margin sediments. Thinking about iron sources rather than iron removal, dissolved [232]Th input rates, estimated by measuring [232]Th and [230]Th together, can be converted into input estimates of dust to the ocean (Hsieh et al., 2011) and of the iron coming out of that dust. Pavia et al. (2020) recently did this in a GEOTRACES process study in the biological "desert" of the subtropical South Pacific. Dust input to this region of the ocean is one of the lowest in the world, so low in fact that Pavia et al. determined that there must be efficient recycling of the dust-derived Fe here in order to support the prevalent levels of the Fe-requisite enzymatic function of nitrogen fixation found in cyanobacteria.

Thorium-based dust estimates still face uncertainties, including assumptions about how much Th dissolves from dust, where exactly in the water column it dissolves, and how exactly to apply Th residence times based on [230]Th. An intercomparison of several methods for estimating dust deposition in the North Atlantic, including aerosols, [7]Be, sediment traps, and thorium, reveal agreement between the methods within about a factor of 5 (Anderson et al., 2016), demonstrating a non-trivial uncertainty that will improve with further development of these methods.

ADVANCES AND FUTURE OPPORTUNITIES

To summarize, we have learned that the thorium stopwatches are useful for quantifying trace element supply and removal terms in the ocean's biogeochemical cycle. Thorium-based estimates have refined iron residence times and iron supply rates from both dust deposition and benthic sediment release. While the role of iron as a limiting nutrient to ocean ecosystems has garnered that element much attention, the thorium isotopes are also helping to constrain the movement of other trace metals, including Cu, Al, and the paleo-proxy Ba as mentioned, as well as other micronutrient metals Co, Cd, and Mn (Black et al., 2019) and the pollutant Pb (Lanning et al., 2023), not covered here.

There is still more to discover about thorium isotope behavior in the ocean, however. The nature of the dust dissolution processes, thorium scavenging itself, and the assumptions behind the paired use of ^{232}Th and ^{230}Th are all still relatively unexplained in terms of mechanistic detail. For instance, ^{230}Th-based ^{232}Th fluxes tend to increase with depth in the upper water column, which is not realistic given a source from dust dissolution in the surface ocean. Dissolved ^{232}Th fluxes can also represent metal supply from margin sediments (Pérez-Tribouillier et al., 2020) in addition to, or in the absence of, dust sources, sometimes creating a disentanglement issue for these sources (Hayes et al., 2022). Ocean biogeochemical modeling of the thorium isotopes is ongoing and has potential to help clarify both removal rate and supply rate issues since these models can now be constrained by the growing GEOTRACES database. Additionally, while it is often assumed that Th adsorbs onto any particulate matter agnostically, marine particle types have systematic variation in size partitioning (Subhas et al., 2023). This size partitioning affects specific surface area for adsorption, as well as the chemical adsorptive capacity of particle types such as organic matter functional groups.

Fundamental surface chemistry modeling and measurements may be helpful in shedding light on these processes that, up until now, have mainly only been investigated through their impacts on radioactive disequilibria.

Nonetheless, the results so far for Th-based fluxes and timescales are clearly pushing toward refining these useful approaches. Next time you have a geochemical question on trace element supply or removal at sea, consider using one of the thorium stopwatches!

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