**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 ($0.4 \times 10^{-15}$ 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 234Th 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 234Th data (Owens et al., 2015), which exhibits a characteristic “deficit” of 234Th 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 234Th-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 234Th stopwatch is well positioned to track this timescale of weeks to months as it approaches 5 times 24 days, or the timescale on which 234Th would return to secular equilibrium.

**TRACING BENTHIC ELEMENT SUPPLY WITH 228Th (AND Ra)**

Moving up in half-life, 228Th 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 228Ra (half-life 5.8 years) undergoes two beta decays and a short-lived intermediary to form 228Th (half-life 1.9 years), which subsequently alpha decays into 224Ra (half-life 3.6 days). In contrast to all Th isotopes, Ra is relatively soluble in seawater. While 228Th:224Ra considerations can be used to quantify particulate scavenging removal (Figure 1; Hayes et al., 2018a) similar to 234Th, we focus here on a different application, using 228Th as the parent isotope rather the progeny.

The 228Th in sediments supplies a constant source of 224Ra to sediment porewaters (Figure 1). Some of that 224Ra escapes into bottom seawater through processes of sediment irrigation and advective flows, and this 224Ra source is demonstrated in the North Atlantic dataset shown in Figure 2 (Charette et al., 2015). The deficit of 224Ra within sediment porewaters with respect to its parent 228Th can further be used to derive a flux of 224Ra 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 224Ra/228Th 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 non-reductive 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...
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 $^{228}$Ra, whose parent is $^{232}$Th (Figure 1; e.g., Sanial et al., 2018), with some slightly different assumptions (Charette et al., 2016).

**TRACING SCAVENGING AND PARTICLE FLUXES WITH $^{230}$Th**

There is a large jump in time to the next longest-lived Th isotope, $^{230}$Th, with its half-life of 76,000 years, but it can provide information on particle sinking rates on longer timescales. Similar to $^{234}$Th, $^{230}$Th is produced in the ocean by another uniformly distributed uranium isotope, $^{234}$U (Figure 1). Once injected into the dissolved phase by alpha decay, $^{230}$Th 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, $^{230}$Th can record events on the timescale of its water column residence rather than on the timescale of its radioactive half-life. In the sediment, $^{230}$Th 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 par-
ticle fluxes are important, for example, for
understanding the ocean’s uptake of car-
bon dioxide and global climate.

As in the case of $^{234}$Th-derived particle
fluxes of Fe, $^{230}$Th can also be used to esti-
mate 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 col-
umn (~2 km), $^{230}$Th-normalized flux on
water column particles is one of the only
methods for estimating a sinking partic-
ulate flux, aside from the traditional tech-
nique of deep-moored sediment traps.

Rahman et al. (2022) used the partic-
ulate $^{230}$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 partic-
ulate organic matter, but it is relatively
well preserved as it sinks in the water col-
umn and is subsequently buried, whereas
almost all of the organic matter tends to
be respired before burial. By compar-
ing 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 mat-
ter 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 sedi-
ments 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 sup-
ply 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 col-
umn 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 spectrom-
etry (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 activ-
ities. Some of the first precise measure-
ments of $^{232}$Th and $^{230}$Th reported in
seawater (Moore and Sackett, 1964)
were made using ~200 liter water sam-
ple, which was roughly the necessary
size sample needed to detect these iso-
topes 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 dissolu-
tion 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 data-
set 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, dis-
solved $^{232}$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 bio-
logical “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. deter-
mined that there must be efficient recy-
cling of the dust-derived Fe here in order
to support the prevalent levels of the
Fe-requisite enzymatic function of nitro-
gen fixation found in cyanobacteria.

Thorium-based dust estimates still
face uncertainties, including assump-
tions 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, sedi-
ment traps, and thorium, reveal agree-
ment between the methods within about
a factor of 5 (Anderson et al., 2016),
demonstrating a non-trivial uncertainty
that will improve with further develop-
ment 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 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 232Th and 230Th are still all relatively unexplained in terms of mechanistic detail. For instance, 230Th-based 232Th 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 232Th 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 radiocative 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 or sea, consider using one of the thorium stopwatches!

REFERENCES


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