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Pa/Th as a (paleo)circulation tracer: A North Atlantic perspective

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Despite complex geochemical ocean cycling, sedimentary Pa/Th ratios provide a method for reconstructing past Atlantic overturning rates. This review highlights progress and challenges from the combination of modern and paleo studies.

Measuring rates of processes in the ocean remains a key target in both modern and paleoceanographic studies. Ocean-driven, cross-equatorial heat transport provides a clear physical link between global climate and regional heat distribution, to the extent that constraining the rates of basin-scale meridional overturning circulation is of importance. The decay of radioactive elements (e.g. tritium, radiocarbon) provides a means for quantifying this overturning, given knowledge of isotopic sources and cycling.

In this article we highlight a particular use of radioactive elements within the uranium-series decay chains. The approach relies on the contrasting chemistry of soluble uranium (U) and two daughter elements, thorium (Th) and protactinium (Pa). Specifically, ^{238}U and ^{235}U occur in nature in a fixed ratio, and ^{238}U decays to ^{230}Th (via ^{234}U), while ^{235}U decays to ^{231}Pa. Since uranium resides in seawater sufficiently long to be very well mixed throughout the ocean, the known concentration and predictable decay rates of each isotope can be used to calculate the production of ^{230}Th and ^{231}Pa. These isotopes are therefore produced with a fixed activity ratio of 0.093. Both daughter isotopes are rapidly adsorbed, or "scavenged", onto marine particles, which subsequently accumulate on the seafloor as sediments. Thorium is scavenged more efficiently than Pa by most types of marine particles, leading to contrasting residence times in seawater, allowing for differential lateral transport and measurable shifts in the Pa/Th activity ratio of underlying sediments. These deviations from the production ratio reflect a balance between scavenging and export from the basin via the overturning circulation. Today, the sediments of the North Atlantic have a Pa/Th ratio of ~0.05 because some Pa is being transported southwards and buried in the Southern Ocean (Yu et al. 1996). This export can also be deduced from analyses of seawater Pa and Th concentrations (Deng et al. 2018, as summarized in Fig. 1). In principle, less water advection should result in less export and therefore enhanced burial of Pa, and higher sedimentary Pa/Th ratios in the North Atlantic.

The use of sedimentary Pa/Th ratios to assess past flow was pioneered in 1996 by Yu et al. who compared Holocene and Last Glacial Maximum sediments from across the Atlantic to test whether there was any change in this ratio associated with the cold, glaciated climate. Surprisingly, the results showed very little difference between modern and glacial overturning in the deep ocean. By contrast, Pa/Th analyzed in rapidly accumulating sediments from the Bermuda Rise indicated that there may have been rather large changes in circulation during the deglaciation (McManus et al. 2004). From modestly increased glacial values, suggesting persistent overall overturning, Pa/Th ratios increased markedly to high values close to the production rate during Heinrich Stadial 1, and to elevated values during the Younger Dryas – interpreted as a reduction in overturning strength. Importantly, these changes occurred in association with North Atlantic iceberg discharge events and northern cooling, pointing to a link between freshwater, climate, and reduced Atlantic overturning. The Bermuda Rise Pa/Th record is now widely used as an archetype circulation record for the North Atlantic, providing a modeling target and general reference curve for many paleoclimate studies (e.g. Liu et al. 2009). Similar associations between climate change and changes in sedimentary Pa/Th have been observed throughout the last glacial and deglaciation in the North Atlantic (Gherardi et al. 2005; Böhm et al. 2015; Henry et al. 2016; Lippold et al. 2009; Ng et al. 2018).

Challenges

The complex geochemical cycling of the uranium-series isotopes adds multiple complications to the use of Pa/Th as a circulation tracer. For example, it has been established that Pa is scavenged more effectively onto opal than it is onto carbonates (e.g. Chase et al. 2002; Luo and Ku 2004). Particle concentration and iron-rich phases are other factors that influence the scavenging efficiency of Pa and Th, so Pa/Th could potentially be affected by changes in productivity, nepheloid layers, or hydrothermal activity (e.g. Bradtmiller et al. 2007; Hayes et al. 2015). Recent paleoclimate studies have assessed both the opal concentration and particle flux rates to investigate their competing influence on sedimentary Pa/Th ratios. For example, Bradtmiller et al. (2014) drew on the approach of Yu et al. (1996) to look at spatial patterns of Atlantic sedimentary Pa/Th in three time-slices, filtering for both opal and particle flux. The average of the North Atlantic data supported the early conclusion of Yu et al. (1996), with no significant difference between modern values and those during the Last Glacial Maximum, although

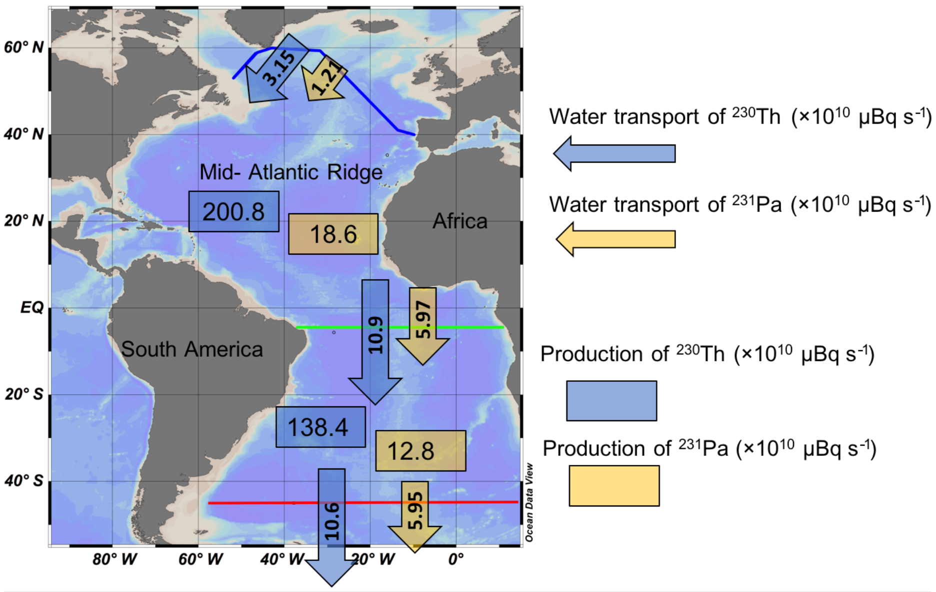

Figure 1: This overview figure reproduced from Deng et al. (2018) shows fluxes of ^{230}Th (blue arrows) and ^{231}Pa (yellow arrows) at three latitudes in the Atlantic. When compared to the total production of ^{230}Th (blue boxes) and ^{231}Pa (yellow boxes) these fluxes indicate that only 4% of the ^{230}Th, but 26% of the ^{231}Pa, produced in the North Atlantic are exported southward by ocean circulation in the modern ocean (Deng et al. 2018). It is this relatively larger export of ^{231}Pa on which the Pa/Th proxy for past circulation relies.

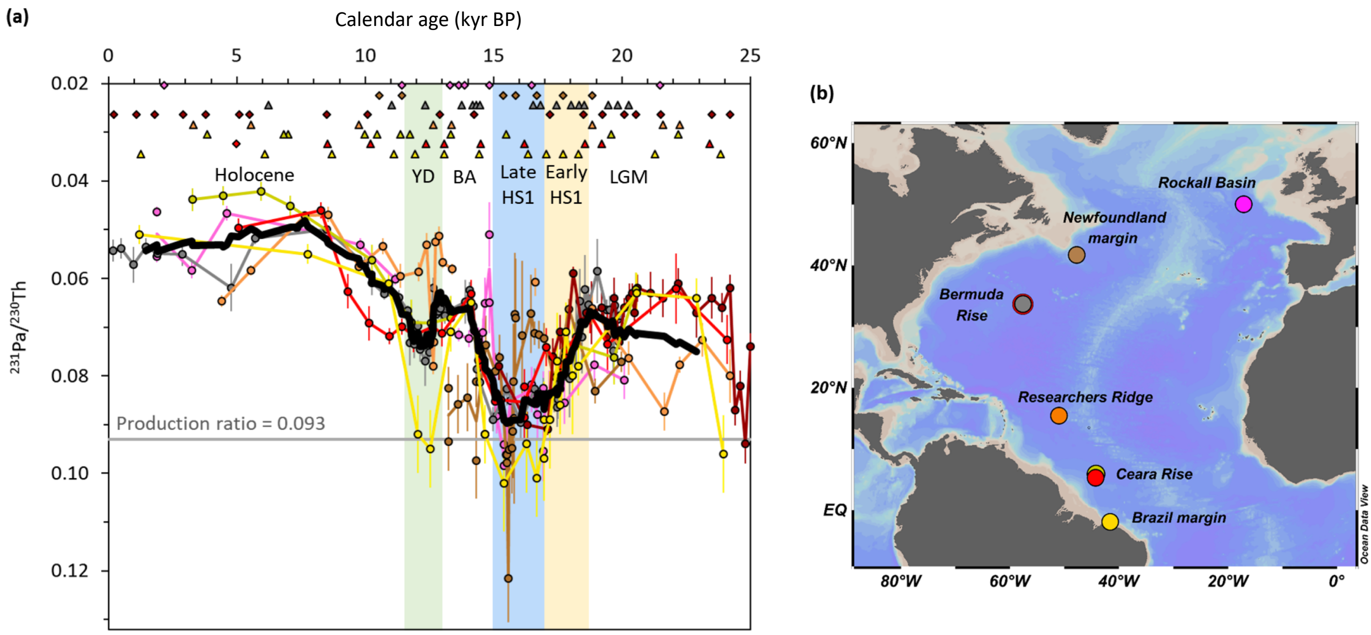

Figure 2: Past changes in AMOC rate over the last 25,000 years. **(A)** Compilation of selected Atlantic sedimentary $^{231}Pa/^{230}Th$ records (Ng et al. 2018). Bold black line is the composite $^{231}Pa/^{230}Th$ record that reflects the average basin-scale changes in circulation rate (Ng et al. 2018); colors correspond to sites identified in **(B)** site map. Error bars represent two standard errors of the mean. Triangle and diamond symbols respectively signify ^{14}C and non-^{14}C chronological tie-points. Annotations of key climate events: LGM: Last Glacial Maximum; HS1: Heinrich Stadial 1; BA: Bølling-Allerød; YD: Younger Dryas (Ng et al. 2018).

spatial and depth differences were apparent. By contrast, the Pa/Th ratio was higher for Heinrich Stadial 1 sediments, consistent with a slowdown in the overall meridional overturning circulation during that time of cold conditions in the North Atlantic.

Modern observations

Important to the principle of using Pa/Th as a tracer for circulation is the deduction that the scavenging of both isotopes is reversible. Both isotopes generally increase in concentration with depth in the ocean, in both dissolved and particulate phases. Bacon and Anderson (1982) explained this behavior with a simple one-dimensional reversible scavenging model. Over the following decades, analysis of additional seawater profiles led to development of more complicated scavenging models with an "advection" component allowing for a quantification of timescales for Atlantic overturning rates ranging from decades to centuries (Moran et al. 2001). A dramatic increase in the number of seawater analyses, modeling studies, and understanding of Pa/Th in the ocean comes from the ongoing international GEOTRACES program (Schlitzer et al. 2018). Although this greater spatial coverage has enabled broadscale estimates of the export of Pa and Th from the Atlantic (e.g. Fig 1; Deng et al. 2018), the expected pattern of a Pa/Th evolution towards higher values as waters travel along the advective pathways of the Atlantic is not apparent in seawater data. These data suggest that there are aspects of the marine chemistry of Pa and Th that are not yet fully understood, and will require further investigation into their sources, sinks, and cycling. Without this understanding, it is challenging to interpret Pa/Th data from a single location. It remains the case, though, that with sufficient cores to characterize the sedimentary ratio of Pa/Th at a basin scale, the net export of Pa can provide powerful information about advection from the basin.

A remaining difficulty in this respect, however, is to robustly interpret sediment data at times when water-mass proxies (e.g. $\delta^{13}C$, Cd/Ca) indicate that there was deep-water flow both into and out of the North Atlantic.

Assessing the basin-scale behavior of Pa/Th in such situations is an important target of ongoing modeling efforts. Early efforts to simulate the behavior of Pa/Th in the Atlantic confirmed its potential sensitivity to changes in overturning circulation rates, including on millennial timescales (Marchal et al. 2000). A subsequent study utilized an inverse method to place constraints on the departures from the observed modern circulation constrained by relatively limited sedimentary data (Burke et al. 2011). More recently, the direct incorporation of Pa and Th in ocean circulation models (e.g. Missiaen et al. 2019) heralds new possibilities for insights derived from comparisons of simulations with both water-column and sedimentary data.

Where are we now?

Despite challenges, there is a clear place for the use of sedimentary Pa/Th in the reconstruction of past circulation rates. By using multiple cores, and by assessing the potential complicating factors from variable scavenging rates, Pa/Th can act as a powerful proxy. Indeed, a recent synthesis of Atlantic deglacial sedimentary cores, filtered for particle and opal flux, yields a coherent pattern over the last 25,000 years (Fig. 2; Ng et al. 2018). In particular, cores from the deep high-latitude North and the West Atlantic all yield broadly similar results as the original high-resolution Bermuda Rise records, emphasizing a strong case for a broad overturning control on the sedimentary Pa/Th ratio, with links to past millennial climate events.

With closer integration of GEOTRACES seawater and core-top sediment data with modeling there is scope to move from general statements on overall overturning rates to a more nuanced interpretation. While quantifying overturning rates may remain challenging, drawing on the strength of these intriguing isotopes has the potential to continue to reveal new information on how and why the oceans have changed in the past.

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