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Title: Ocean mixing and ice-sheet control of last deglacial seawater $^{234}$U/$^{238}$U evolution

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Abstract: Seawater $^{234}$U/$^{238}$U provides global-scale information on continental weathering and is vital for marine U-series geochronology. Previous evidence supports an increase in $^{234}$U/$^{238}$U since the last glacial, but the timing and amplitude of its variability was poorly constrained. Here we report two seawater $^{234}$U/$^{238}$U records based on well-preserved deep-sea corals from the low latitude Atlantic and Pacific. The Atlantic $^{234}$U/$^{238}$U starts to increase before major sea level rise and overshoots the modern value by 3‰ in the early deglaciation. Deglacial $^{234}$U/$^{238}$U of the Pacific converges with the Atlantic after the abrupt resumption of Atlantic meridional overturning. We suggest that ocean mixing and early deglacial release of excess $^{234}$U from enhanced subglacial melt activity of the Northern Hemisphere ice sheets have driven the observed $^{234}$U/$^{238}$U evolution.
**One Sentence Summary:** Well constrained seawater $^{234}$U/$^{238}$U evolution provides evidence of less efficient inter-ocean mixing and enhanced subglacial melt activity early in the last deglaciation.

**Main Text:** The last deglaciation (18.0-10.5 ka, thousand years ago) saw massive changes in the Earth’s surficial environments including temperature and precipitation, as well as the retreat of the Northern Hemisphere (NH) ice sheets and sea-level rise (1, 2). These processes have the potential to induce large variability of weathering of the upper continents and the composition of chemical fluxes to the ocean. The ratio $^{234}$U/$^{238}$U is one of the isotopic signatures with potential to record global changes in continental weathering during this critical climate transition (3).

The activity ratio of $^{234}$U to $^{238}$U in the modern seawater is ~15% higher than secular equilibrium (4), due to the relative mobile nature of $^{234}$U induced by $\alpha$-recoil effects (5) in the weathered host rocks. $^{234}$U is enriched relative to $^{238}$U at particle boundaries or damaged lattices, and is expected to be preferentially released in the initial phases of weathering (6). Leaching experiments (7) support that the early fraction of granite leachates is high in both U concentration and $\delta^{234}$U ($\delta^{234}$U = ($^{234}$U/$^{238}$U activity ratio -1)*1000). In the last glacial period, subglacial drainage of meltwaters from a limited area of ice sheet interior to the margins may have been possible (8), analogous to the Antarctic Ice Sheet today where basal meltwater is routed to the margins via subglacial channels (9). Nevertheless, a large fraction of the glaciated NH continents likely had very limited chemical weathering flux to the ocean due to widespread freezing conditions of the ice-sheet base (10). It is reasonable to assume that a labile pool of excess $^{234}$U due to $\alpha$-recoil would have accumulated in the frozen sediments or isolated subglacial lakes/ponds in the wet-based zones under these ice-sheets. In fact, high dissolved $\delta^{234}$U of up to ~4000‰ has been observed in the Antarctic Taylor Valley (11), a region thought to be hydrologically connected to the nearby ice sheets (12). In the non-glaciated regions, $\delta^{234}$U released from weathering would also respond to tectonic and precipitation changes (3). A reliable reconstruction of oceanic $\delta^{234}$U thus offers a potentially important route for tracing global scale weathering variability during climate transitions.

The long residence time of U in seawater (~400 ky, thousand years (13, 14)) would lead to the expectation that any equilibrium response to external inputs should be more than an order of magnitude longer than the deglacial time scale (~10 ky). However, a growing number of studies have inferred that seawater $\delta^{234}$U might have been lower during the last glacial than
the Holocene and previous interglacials (3, 15-17), and might have also changed on millennial time scales (18). These observations imply that there have been large, relatively rapid changes in the U isotope budget of the ocean, and are supported by an updated compilation of published coral initial $\delta^{234}U$ data over the last 30 ka (Fig. 1a). However the extensive scatter in the data which is likely due to diagenesis (19) has limited the ability to constrain the timing and magnitude of $\delta^{234}U$ variations through time.

To put more robust limits on seawater $\delta^{234}U$ evolution and infer past changes in chemical weathering, we report two well-constrained U isotope records based on well-preserved deep-sea corals recovered from the low latitude North Atlantic and the Pacific Galápagos platform over the last 30 ka (Fig. 1b, S1, S2), with additional samples for reference from 50-30 ka (19) (Fig. S3). The general trend of $\delta^{234}U$ evolution agrees with previous studies (3, 15-17), although the new glacial deep-water corals tend to exhibit higher $\delta^{234}U$ than the surface corals in each ocean basin (Fig. S3). Our data thus suggest a somewhat smaller glacial-Holocene $\delta^{234}U$ difference of only 3-4‰ (Fig 1). Atlantic $\delta^{234}U$ started to increase at around 22-20 ka (Fig. 1b), followed by a rapid increase of ~6‰ up to 150‰ during Heinrich Stadial 1 (HS1, 18.0-14.6 ka). Available Pacific data are less well resolved, but exhibit lower $\delta^{234}U$ values than the Atlantic during early HS1. The $\delta^{234}U$ of Atlantic and Pacific records converged to the modern level during the Bølling-Allerod (B-A: 14.6 – 12.9 ka). Prior to the last glacial maximum (25-50 ka) our dataset is consistent with a lower $\delta^{234}U$ than the Holocene (Fig. S3), but it is not well enough resolved to identify potential millennial scale changes (18).

There are several possible causes for the observed deglacial seawater $\delta^{234}U$ increase. Coastal regions have been inferred to retain U with high $\delta^{234}U$ during sea-level highstands (16). Redissolution of the coastal U has been hypothesized to drive $\delta^{234}U$ increase when sea level rises (16). If so, seawater $\delta^{234}U$ is expected to increase closely following sea-level rise. The increase in Atlantic $\delta^{234}U$ is expected to increase closely following sea-level rise. The increase in Atlantic $\delta^{234}U$ does appear to coincide with the initiation of the sea level rise (Fig. 2), but most of the $\delta^{234}U$ increase occurred before the major sea-level rise in the late deglaciation. Hence we suggest that although U stored in the coastal areas could be important for $\delta^{234}U$ variability in other situations (18), it was probably not the main driver of the deglacial $\delta^{234}U$ evolution. An increase in deep water oxygenation may release redox sensitive U from the seafloor sediments, possibly affecting seawater U budget during deglaciation. The early deglaciation is thought to have had lower oxygen concentrations than the modern day in the upper ocean (e.g., <1.5 km) (20). Increased bottom water oxygenation in the Atlantic and
deep Pacific only occurred after HS1 (20) with resumption of North Atlantic deep overturning (21), which occurred later than the observed increase in $\delta^{234}$U. Together, these results suggest that external sources with excess $^{234}$U or ocean mixing have to be involved to explain the observed $\delta^{234}$U variability.

Models (22) and proxies such as $^{231}$Pa/$^{230}$Th (21, 23) support a reduced deep Atlantic Meridional Overturning Circulation (AMOC) (Fig. 2) as well as reduced surface Gulf Stream (24) and Agulhas leakage (25) during HS1. These processes likely resulted in an upper Atlantic that was more isolated from the rest of the ocean than it is today (19). Increased isolation of the upper Atlantic (~2.0 km, including the depth range of the deep sea corals in this study) would act to reduce the effective uranium residence time, and allow its $\delta^{234}$U to change more rapidly than in the Pacific. We applied a two-box model, consisting of an upper Atlantic-Arctic box and a ‘rest-of-the-ocean’ box, to study the influence of changing external sources and changing ocean circulation on seawater $\delta^{234}$U (19). Modern high-latitude riverine inputs have significantly higher $\delta^{234}$U than middle to low latitude inputs and mainly supply the Arctic and polar North Atlantic (19). If the $\delta^{234}$U and U fluxes of all external sources are kept constant throughout the last 25 ky, our model result (Fig. 3a) shows that a slowdown of ocean circulation during HS1 can result in a resolvable difference of $\delta^{234}$U between the upper Atlantic and the rest of the ocean, depending on the degree of reduction in exchange flux. This result is consistent with the difference in $\delta^{234}$U between the Pacific and Atlantic $\delta^{234}$U records (Fig. 1) and contrasts with the general assumption that U isotopes are homogenous throughout the global ocean (i.e., difference no larger than 0.4‰ (4)). Our result also raises the possibility that other isotope systems with relatively long residence times might exhibit differences between different ocean basins during periods of reduced ocean mixing.

Ocean circulation, however, cannot account for the overall glacial-interglacial ~3‰ or more increase in $\delta^{234}$U of both ocean basins (Fig. 3a). External $^{234}$U inputs must have increased relative to $^{238}$U during the early deglaciation. With 3 times the modern riverine U flux, a 3‰ shift in oceanic $\delta^{234}$U is possible during HS1 (Fig. S4). However since the hydrological cycle was probably weaker during the late last glacial and early deglaciation than the present (2), increased dissolved U flux from global rivers alone as a driver for the $\delta^{234}$U change is considered unlikely. An increase in $\delta^{234}$U of the continental inputs is, therefore, likely to have been important in seawater $\delta^{234}$U evolution. There are no direct measurements of the $\delta^{234}$U of past watersheds, so here we compiled $\delta^{234}$U data from speleothems that grew during the relevant time period. Although speleothem $\delta^{234}$U does not necessarily reflect the primary
surface weathering signal, including influences such as the percolation of meteoric waters from the surface down into the cave, it may still provide a first order indication on the variability of hydrological cycle that controlled the overall $^{234}$U budget available for weathering (26). The available data come from the mid to low latitudes (Fig. S5) and they do not exhibit any distinctive $\delta^{234}$U shifts from 30-15 ka, suggesting that weathering variability in these areas was not large enough to account for the oceanic $\delta^{234}$U observations.

Instead, high-latitude processes could have played a key role in driving global seawater $\delta^{234}$U increase from the last glacial to 15 ka. In the early part of the last deglaciation, the base of North American ice sheets are thought to have become increasingly wetter (10). We propose that $^{234}$U-enriched water was released from subglacial melt reservoirs with a prolonged residence time and from leaching of the previously frozen subglacial sediments by basal melt water over this period. In both cases, subglacial meltwaters are likely to be enriched in recoiled $^{234}$U (7, 11). In addition, sediments (and their former pore waters) frozen within the base of icebergs might also contribute to releasing U and nutrients to the ocean (27) during these periods. The reconstructed number of ice streams based on field evidence (8) and the modelled subglacial melt rate (10, 28) (Fig. 2b) of the North American ice sheets were much higher during early deglaciation (before 15 ka) than later. It is notable that the modelled ice discharge (29) of the Laurentide Ice Sheet was also high during the glacial and early deglaciation, reaching a peak at the late HS1 (Fig. 2). This timing is consistent with the enhanced release and transport of excess $^{234}$U to the ocean during the early deglaciation. In this case the peak oceanic $\delta^{234}$U indicates that active basal water from the whole ice-sheet interior may have been active in exporting to the margin during HS1. In another modelling experiment (19), the sensitivity of oceanic responses to inputs with different $\delta^{234}$U ratios was tested. With an average $\delta^{234}$U of $\sim$800‰ for the input to the upper Atlantic during HS1, the model result is able to reproduce the observed amplitude of $\delta^{234}$U increase from the last glacial to 15 ka (Fig. 3b). A more realistic case might be an increase in both the U flux and the $\delta^{234}$U of the high-latitude continental inputs, but de-convolving these two factors is difficult. There is a hint from the compiled data that the surface ocean has lower $\delta^{234}$U than the intermediate depth ocean (Fig. S3). Our extended modelling experiments are unable to replicate this feature, even with all high-latitude excess $^{234}$U routed to the intermediate ocean via the polar surface Atlantic and no deep-ocean overturning and mixing (19). These results indicate that other mechanisms such as local influences or diagenetic processes are responsible to those differences.
The transition from HS1 to B-A is marked by a distinct decrease in $\delta^{234}$U of the low latitude Atlantic by $\sim$3‰ from about 150‰ to the modern seawater signature. The Pacific $\delta^{234}$U appears to rise at the same time, converging with the Atlantic $\delta^{234}$U during mid B-A. We suggest this convergence is due to the abrupt increase in overturning of the Atlantic at the end of HS (21, 23) (Figs 2c and 3a), although the depletion of subglacial excess $^{234}$U pool might also have played a role (19). Stabilized Holocene seawater $\delta^{234}$U afterwards implies that U cycle in the modern ocean is likely close to a steady state (30). Nevertheless, perturbation of oceanic U isotopes by polar processes might still be active even during the climatically and oceanographically more stable late Holocene period. For example, widespread collapse of the Ross Ice Shelf and export of old materials from inland of Antarctica was inferred to occur at $\sim$5-1.5 ka in response to the regional warming (31). These may be accompanied by a $^{234}$U rich flux to the Southern Ocean, although a large shift in the whole ocean $\delta^{234}$U was probably limited. On longer orbital time scales, seawater $\delta^{234}$U is thought to be higher during past interglacial periods and lower during glacials (e.g., (3, 16, 17)) with the decreases potentially associated with low sea level (16). By comparison to the deglacial mechanism, our study implies that progressive NH glaciation could have reduced the weathering input from high latitude continents, leading to lower glacial oceanic $\delta^{234}$U.

The retreat of the NH ice sheets started at about 20 ka and continued through HS1 (Fig. 2a) (1), considerably earlier than enhanced surface melting that dominated ice-sheet mass loss and sea level rise in the late deglaciation/early Holocene (29). Our data provide evidence for enhanced subglacial melt activity from the NH ice-sheet interior during the early deglaciation, supporting the notion that basal melting/sliding represents one of the feedbacks involved in enhancing early deglaciation as a result of the build-up of very large NH ice sheets (10). An interesting consequence of the basal melt inputs may be the associated release of nutrients to the ocean. Recent work from the Greenland Ice Sheet indicates dissolved phosphorus yields are at least equal to those associated with the Mississippi or Amazon rivers (32). In this regard, nutrients from direct subglacial weathering should be considered in the future as a potential source to fuel productivity in the North Atlantic during HS1.

References and Notes:

19. Materials and methods are available as supplementary materials on Science Online.
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Figure Captions:

Figure 1 Seawater $\delta^{234}$U evolution reconstructed from corals over the last 30 ky. (A) Compilation of published coral initial $\delta^{234}$U within the range of 135‰ to 155‰ and with 2 sigma error <3‰ (19). Data outside of this range have been truncated. (B) Low latitude North Atlantic records with ± 2 sigma confidence lines. Also shown are the initial $\delta^{234}$U of low latitude Pacific reconstructed from Galápagos deep-sea corals. One data point of Galápagos coral during B-A with initial $\delta^{234}$U higher than 155‰ has likely experienced diagenesis and is not shown. Black dotted line marks the modern seawater signature.

Figure 2 Seawater $\delta^{234}$U evolution compared with other climate records. (A) Retreat rate of the northern and southern hemisphere ice sheets (33). (B) Basal melting rate of the North American ice sheets (28) and the ice discharge of the Laurentide ice sheet (29). (C) $^{231}$Pa/$^{230}$Th of North Atlantic deep sediment core (21, 23). (D) Sea-level history (34). (E) Our reconstructed $\delta^{234}$U evolution in the upper Atlantic and Pacific. Black dotted line denotes modern seawater $\delta^{234}$U.

Figure 3 Sensitivity experiment for seawater $\delta^{234}$U response to ocean circulation and external inputs. (A) Effect of ocean mixing slowdown alone. (B) Effect of variable $\delta^{234}$U of inputs to the upper Atlantic, applying 50% reduction of the glacial exchange flux during HS1. The area between the dash-dot curves is the range of low latitude Atlantic $\delta^{234}$U. External U fluxes through time in both experiments are kept as the modern inputs.
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