Temporal Relationships of Carbon Cycling and Ocean Circulation at Glacial Boundaries

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Evidence from high-sedimentation-rate South Atlantic deep-sea cores indicates that global and Southern Ocean carbon budget shifts preceded thermohaline circulation changes during the last ice age initiation and termination and that these were preceded by ice-sheet growth and retreat, respectively. No consistent lead-lag relationships are observed during abrupt millennial warming events during the last ice age, allowing for the possibility that ocean circulation triggered some millennial climate changes. At the major glacial-interglacial transitions, the global carbon budget and thermohaline ocean circulation responded sequentially to the climate changes that forced the growth and decline of continental ice sheets.

Records of past global climate preserve evidence of large-scale changes in temperature and ice volume at glacial-interglacial boundaries. Although the timing of ice ages is broadly driven by Milankovich orbital cycles, the small insolation changes require amplifying mechanisms to produce the large glacial-interglacial climate changes. Fluctuation in North Atlantic Deep Water (NADW) production is a potential amplifier and has been suggested as a trigger for rapid global climate shifts (1). Carbon dioxide (CO₂) is another possible amplifier on glacial-interglacial time scales, because its atmospheric concentration is predominantly controlled by changes in deep-ocean storage (2) and the terrestrial carbon reservoir (e.g., 3–5). Carbon isotope ratios are distinct in different reservoirs, making it a powerful tool to constrain the timing of global carbon budget reorganizations relative to other changes in the climate system. In the oceans, carbon isotope ratios of benthic foraminifera (benthic δ¹³C) are commonly used as a proxy for ocean circulation because they vary systematically in water masses [e.g., (6–8)]. However, temporal benthic δ¹³C changes at any location reflect a combination of the global carbon mass balance, ocean-circulation changes, air-sea equilibration, and productivity changes. If carbon budget and ocean-circulation signals can be deconvolved, the temporal sequence of major shifts in global ice volume, carbon mass balance, and ocean circulation can help to clarify the ocean’s role as a trigger of, or a response to, major climate changes. In this study, we compare the temporal sequence of these changes since the last interglacial period. Chronological ambiguities are obviated through study of different proxy signals in the same core, and thus the sequence of events associated with climate change and ocean circulation can be extracted.

Nd isotopic systematics. We use Nd isotopes as a proxy of the balance between NADW and southern-sourced waters in the South Atlantic. ¹⁴⁴Nd/¹⁴²Nd ratios vary in the

References and Notes

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Supporting Online Material

www.sciencemag.org/cgi/content/full/307/5717/1928/ DC1 Materials and Methods
Fig. S1
Tables S1 and S2
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Earth as a result of the $^\alpha$ decay of $^{147}$Sm ($t_{1/2} \sim 106 \times 10^9$ years), and in the oceans, the values reflect the age of the continental sources of dissolved Nd (9). The utility of Nd isotopes as a paleocirculation proxy stems from its variability in the oceans. In seawater and Fe-Mn nodule and crust surfaces, Nd isotope ratios geographically vary over a large range from $\varepsilon_{\text{Nd}} < -20$ in the Labrador Sea to values as high as $\varepsilon_{\text{Nd}} \sim 0$ in the northwest Pacific (10). Unlike low-mass stable isotope and element ratios, Nd isotope ratios do not show measurable mass-dependent fractionation by biological and low-temperature processes (11). Nd isotopes are conservative in seawater unless new Nd is added along the transport path. Water-column profiles show that water masses conserve the Nd isotopic fingerprint of the dissolved Nd source regions over long transport paths. For example, the NADW Nd isotope signature ($\varepsilon_{\text{Nd}} \sim -14$) can be traced into the South Atlantic, and the Antarctic Bottom Water (AABW) signature ($\varepsilon_{\text{Nd}} \sim -7$ to $-9$) can be traced northward in the Atlantic (9, 12, 13).

The Nd isotopic signal of deep-water masses can be preserved at submillennial time resolution in the Fe-Mn oxide fraction of deep-sea cores, and recent studies found Nd isotopic variability in the oceans on glacial-interglacial and millennial time scales (14–18).

This study focuses on cores RC11-83 (40°36'S, 9°48'E, 4718 m) and TNO57-21 (41°08'S, 7°49'E, 4981 m) from the Cape Basin, southeast Atlantic (tables S1 and S2), whose chronology is based on radiocarbon ages and spliced stable isotope stratigraphy (8, 18–20). High sedimentation rates (~20 and ~15 cm/1000 years, respectively) allow subcentury-scale temporal resolution. An initial application of Nd isotope ratios of Fe-Mn leachates in RC11-83 at orbital time resolution (15) showed that the NADW signals were stronger during warmer climate intervals and weaker during cold intervals through the last ice age. These variations were subsequently confirmed in a Holocene to Last Glacial Maximum (LGM) profile of core MD96-2086 from the northern Cape Basin (16, 21). Our more detailed studies of RC11-83 and TNO57-21 show fine-scale variability that parallels other climate proxies (18) (Fig. 1). The previous studies include extensive discussions of evidence that Nd isotope ratios in the Fe-Mn oxide leachates of these cores reflect deep seawater (15, 16, 18, 22). In RC11-83/ TNO57-21, Sr isotope ratios are indistinguishable from Quaternary seawater ($^{87}\text{Sr} / ^{86}\text{Sr} \sim 0.7092$) and much lower than associated terrigenous detritus ($0.717$ to $0.723$) (23). This precludes detrital contamination of the leached Sr. Nd is less likely to be contaminated by the detritus, because it is much less soluble than Sr. Moreover, bottom-water SiO$_2$ concentrations (24) and core top leachate Nd isotope ratios are consistent with $\varepsilon_{\text{Nd}}$SiO$_2$ covariances of present-day Atlantic seawater (15).

Climate transitions. During Marine Isotope Stages (MIS) 1 and 5, Nd isotopes are the most NADW-like (Fig. 1), whereas during MIS 2 and 4 (full glacial stages), values shift beyond modern Southern Ocean values of $\varepsilon_{\text{Nd}}$ ~ $-7$ to $-9$ (9), indicating that the Southern Ocean was more Pacific-like than today. Major Nd isotope shifts occurred at the MIS 5a/4 and 2/1 boundaries. Millennial excursions occur between MIS4/5 and the LGM, corresponding in timing and form to Greenland interstadials 3, 4, 8, 12, 14, and 17 on the basis of comparison to Greenland ice cores $\delta^{18}$O records (25–27). Piotrowski et al. (18) discuss the detailed temporal relationships between changes in Nd isotope ratios and Greenland ice $\delta^{18}$O during the most recent deglaciation. For example, there is increased NADW during the Bolling warming, a decline during the Allerød cooling, and an increase from the Younger Dryas minimum (labeled YD; see Fig. 1B) to the early Holocene. In contrast, there is no corresponding effect during the Antarctic Cold Reversal (ACR). These associations demonstrate a strong linkage between Northern Hemisphere climate variability and the Nd isotope ratios of South Atlantic deep waters.
The covariation of the temporal patterns of benthic $\delta^{13}C$ and Nd isotopes on long-term and millennial time scales (Fig. 1) confirms earlier conclusions that the benthic $\delta^{13}C$ pattern mimics ocean-circulation changes (8, 19, 20). However, the magnitude of the benthic $\delta^{13}C$ changes over glacial-interglacial cycles are too large to have been caused entirely by water-mass mixing. The mean $\delta^{13}C$ of the deep ocean reflects the climate-forced partition of carbon between terrestrial and ocean carbon reservoirs. The deep ocean $\delta^{13}C$ was 0.46‰ to 0.32‰ lower during ice ages than today (28–30), likely caused by increased storage of $\sim$500 gigatons of terrestrial organic carbon ($\delta^{13}C \sim -25‰$) in the ocean (31). The interglacial to glacial benthic $\delta^{13}C$ shift of $\sim -0.8‰$ in RC11-83/TNO57-21 overshoots the glacial Pacific end member by $\sim -0.4‰$ (32–34), which reflects additional productivity and perhaps air-sea exchange and local pore-water effects in the Southern Ocean (35).

To isolate the noncirculation effects on the benthic $\delta^{13}C$ signal, we use Nd isotopes to monitor thermohaline circulation and interpret the $\delta^{13}C$ shifts that are unsupported by the Nd isotope record as caused by noncirculatory effects. A cross-plot of the entire data set is compared to Holocenic and glacial binary mixing curves for global end-member water masses (Fig. 2A). The Nd isotope ratios fall between the NADW and Pacific end members throughout, whereas the $\delta^{13}C$ data lie below the mixing lines and shift toward the glacial Pacific value during glacial climate. The NADW-Pacific mixing lines are an over-simplification of the ocean-circulation system (Fig. 2), which we regard as reference lines allowing a first-order evaluation of large noncirculation effects on Southern Ocean $\delta^{13}C$. They assume that the temporal variability of the Nd isotope ratios is not controlled by shifts in the end-member water masses. Our previous studies extensively discuss the current constraints on the Pacific and North Atlantic end members (15, 18) and are only summarized here. There is strong evidence for stability of Nd isotope ratios of deep Pacific seawater (36). Constraining the Nd isotope ratio of NADW through time is more problematic because of encroachment of AABW into the North Atlantic during cold climate and shallowing of northern-sourced deep waters and the failure of Fe-Mn oxides leached from many North Atlantic cores to yield marine Sr isotopes ratios (37). Rüther et al. [figure 2a in (15)] addressed the issue indirectly by comparing bottom-water SiO$_2$ concentrations (24) and Nd isotope ratios in global Fe-Mn nodules and crusts with the modern seawater-dissolved SiO$_2$-Nd trend. Samples from Fe-Mn nodules and crusts represent average ambient water values over 10$^5$ to 10$^6$ years, encompassing several glacial cycles. Most of the North Atlantic data lie on the modern SiO$_2$-Nd trend, indicating a roughly constant NADW Nd isotope signature. Recent suggestions that the Nd isotope signature of glacial NADW may have been lower (e.g., 38–40) than the present day would not affect our primary conclusions (41).

Further insights into the Nd isotope-benthic $\delta^{13}C$ relationships are gained by separating the data into discrete time slices. Although all the data (Fig. 2A) show a negative correlation, the glacial-interglacial transitions (MIS 5a/4 and LGM-Holocene) data outline a “parallelogram” (Fig. 2B), and those from the MIS 4/3 through the LGM fill its gap (Fig. 2C). Further examination shows that the parallelogram reflects the temporal relationships between Nd and carbon isotope shifts. For example, the data associated with the last deglaciation (Fig. 3A) exhibit a two-stage change. The LGM to Bølling warming data lie on a steep trend, because the $\delta^{13}C$ undergoes a major change toward its Holocene range, whereas the Nd isotopes show a small shift. The benthic $\delta^{13}C$ increases by 0.8‰, representing 90% of the total LGM to Holocene shift, whereas the Nd isotopes decrease by $\sim -0.6\epsilon_{Nd}$ units, representing only $\sim 15\%$ of its total shift. The shallow trend of the post-Bølling data reflects the major glacial-interglacial Nd isotope shift occurring after the benthic $\delta^{13}C$ had already shifted to the interglacial mode. These observations indicate that the $\epsilon_{Nd}$-$\delta^{13}C$ coupling before the Bølling warming was distinct from that afterward. The pre-Bølling interval was associated with substantial climate amelioration and glacial retreat in Europe (42). The data indicate that for $\sim 1500$ years before the Bølling warming (43), initial melting of the continental ice sheets was associated with large changes in the deep-water $\delta^{13}C$ and small variations in deep-water circulation.

Deep-water $\delta^{13}C$ shifted before the Bølling warming, at which time it had already attained its Holocene composition. After the Bølling warming, benthic $\delta^{13}C$ was primarily affected by changes in the balance of the water masses. The shallow slope of the mixing curves (Fig. 2) illustrates that Nd isotopes are a more sensitive proxy for water-mass mixing than benthic

![Fig. 2. Cross-plot of Nd isotope data and benthic $\delta^{13}C$ of RC11-83/TNO57-21. (A) The entire 100,000-year record. (B) Only the glaciation (MIS 5a-4) and deglacial (LGM-Holocene) transitions. (C) Only glacial interstadial events (within MIS 3 and early MIS 2). Simple binary mixing curves are shown between NADW and Pacific (PAC) isotopic end members for the Holocene and the LGM; the $\delta^{13}C$ difference between them is the 0.4‰ mean ocean $\delta^{13}C$ difference (28–30) due to ocean-biosphere carbon budget change (31). The Nd isotopes and benthic $\delta^{13}C$ recorded by RC11-83/TNO57-21 are monitoring the relative mixing proportion of NADW and Pacific-sourced waters in the Southern Ocean (changes in which should parallel the mixing reference curves), whereas benthic $\delta^{13}C$ is also affected by noncirculatory carbon budget changes. Dashed arrows show sequential Nd isotope-benthic $\delta^{13}C$ changes relative to general ocean mixing (Fig. 3). NADW-Pacific mixing curves are based on the following parameters. For the Holocene end members, $-\text{NADW}: \epsilon_{Nd} = -13.5, \text{Nd} = 21$ pmol/kg, $\delta^{13}C = 1.1$, dissolved CO$_2 = 2175$ umol/kg; Pacific: $\epsilon_{Nd} = -4$, Nd = 40 pmol/kg, $\delta^{13}C = 0.0$, dissolved CO$_2 = 2350$ umol/kg. For the Glacial end members, NADW: $\delta^{13}C = 0.6$; Pacific: $\delta^{13}C = -0.5$; all other parameters are the same. Mixing curves are based on (32–34, 48–57). Benthic $\delta^{13}C$ are from (8, 19, 20, 32).]
δ²¹³C. The Bolling warming to Holocene trend nearly parallels the NADW-Pacific mixing lines, whereas LGM to Bolling warming data comprise a steeper slope (Fig. 3A). This is why Nd isotopes record a large Younger Dryas change, whereas Charles et al. (8) found only a hint of a benthic δ¹³C change. During the Younger Dryas, the range of εNd values approaches that of the entire shift from the LGM to the Holocene without a comparable benthic δ¹³C shift (Fig. 3A). A 20% reduction of NADW after the Bolling warming produces an increase in the Nd isotope ratio of ~2 εNd units, with only a ~0.2% change in δ¹³C.

The sequence of events during the last interglacial-glacial transition (MIS 5a to 4) is identical to the deglacial sequence, with benthic δ¹³C shifting toward glacial values before Nd isotopes (Fig. 3B), manifested by a steep trend followed by a shallow one, a mirror image of the deglacial transition. In the initial steep trend, the decrease in benthic δ¹³C values is equal in magnitude to the deglacial shift, without a significant change in Nd isotope ratios. Subsequently, a rapid εNd shift occurred, resulting in the shallow trend, consistent with a reduction in NADW intensity. The MIS 5a/4 NADW shift lags the benthic δ¹³C shift by ~2,500 years (corresponding to 27 cm in TNO57-21). As discussed above for the Younger Dryas, water-mass mixing dynamics is also responsible for the small δ¹³C change compared with the natural scatter that accompanies the abrupt Nd isotope shift during the MIS 5a-4 transition (Fig. 4).

The comparisons of Nd and benthic carbon isotopes have important implications for the sequence of events at major climate transitions. The data indicate that during the last glacial and deglaciation, major changes in South Atlantic deep-water δ¹³C occurred prior to major changes in the global overturning circulation. Significant variability in Nd and benthic δ¹³C also occurred during the millennial Dansgaard-Oeschger (D-O) interstadials of MIS 3 and early MIS 2 (Fig. 1), which fill the parallelogram formed by the glacial-interglacial transitions (Fig. 2 and Fig. 3C). During interstadials, the data shifts directly from full glacial values (higher εNd and lower δ¹³C) toward the NADW end member, although there is some scatter. Here, the carbon and ocean-circulation changes do not display a consistent two-stage lead-lag relationship as during the main glacial-interglacial transitions (Fig. 3C). This simple relationship shows that benthic δ¹³C and Nd isotopes were responding synchronously to circulation changes during MIS 3 and early MIS 2, which (unlike the glacial-interglacial transitions) may allow for a causal role for ocean circulation to trigger the interstadial warmings.

It is unlikely that the consistent benthic δ¹³C lead over εNd at the glacial-interglacial boundaries was produced by bioturbation or diagenesis. The benthic δ¹³C record was generated on Cibicides wu¨llerstorfi, which live at or above the sediment-water interface. Processes that might affect the relative position of benthic δ¹³C and εNd changes include seawater intrusion into sediment porewaters, bioturbation, and postdepositional smearing of the Fe-Mn oxides. Precipitation of Fe-Mn oxides from bottom-water-derived porewaters at depth within the sediment column would cause the Nd isotope record to lead, rather than lag, the benthic δ¹³C record, opposite to what we observe. Bioturbation could cause downward mixing of foraminifera relative to other substrates containing Fe-Mn oxide coatings. If this occurred, the depth difference would have to be >20 cm (the lead-lag depth difference of glacial-interglacial Nd and benthic δ¹³C changes), which is highly unlikely. The overall RC11-83/TNO57-21 εNd and benthic δ¹³C profiles (Fig. 1) give strong evidence against smearing of Fe-Mn oxides generating the lag in Nd isotope changes during the transitions. First, the glacial-interglacial changes are abrupt. Second, there is no lead-lag relationship during millennial fluctuations throughout the record. During most millennial events, benthic δ¹³C εNd covary on centimeter scales [e.g., the “false start” at 15.5 thousand years before the present (ky cal. B.P.), 277 cm (8)]. We conclude that the carbon and Nd isotope data and their lead-lag relationship at major stage boundaries reflect bottom-water chemistry changes at this site.

Temporal relationships. The temporal relationship between the benthic δ¹³C and Nd isotopes indicates that the δ¹³C of the deep South Atlantic shifted by 0.8% during glacial-interglacial transitions at ~1000 to 3000 years before changes in the balance between northern- and southern-sourced waters. The abruptness of the early benthic δ¹³C shifts strongly indicates that they include both the glacial-interglacial mean ocean carbon isotope change of ~0.4% (28-30) and an additional ~0.4% reflecting processes related to Southern Ocean productivity or air-sea equilibration of carbon isotopes. If the mean ocean and Southern Ocean δ¹³C shifts occurred separately, the record would show two steps rather than the single abrupt shift seen clearly during the last interglacial-glacial transition (Fig. 4). Moreover, all other ~0.4% δ¹³C shifts are supported by Nd isotopes changing and, therefore, are attributable to circulation change. Although we are currently unable to quantitatively separate the different noncirculatory effects on the δ¹³C record, the data strongly indicate that the Southern Ocean and mean ocean δ¹³C changed simultaneously and before ocean circulation.

As the mean ocean δ¹³C change was caused by redistribution of terrestrial biosphere and deep-ocean carbon, the relationship between δ¹³C and Nd isotopes during the MIS 2/1 and 5/4 transitions implies that the transfer of isotopically light terrestrial
carbon between these reservoirs occurred prior to the shift between glacial-interglacial modes of ocean circulation. Because the terrestrial biosphere primarily responds to climate change, this strongly indicates that glacial-interglacial climate change occurred before changes in thermohaline circulation. The sequence of events during the MIS 5/4 transition can be shown by using benthic δ18O, benthic δ13C, and Nd isotopes to constrain the timing of ice-sheet growth and deep-water temperature, budget changes, and thermohaline circulation, respectively (Fig. 4). The growth of continental ice sheets is the primary cause of the benthic δ18O change (32), which occurs first and is followed by a large benthic δ13C shift (32) a few thousand years later, which is then followed by the Nd isotope shift. Colder deep-water temperatures causing a large portion of the glacial-interglacial δ18O shift is also consistent with the establishment of glacial conditions concurrent with still-strong Atlantic overturning, followed by a reduction of thermohaline circulation (44). The sequence of events for the last deglaciation is not as easily seen because of complex millennial-scale variations, although the early deglacial carbon shift compared with the Nd isotope shift shows up well in the benthic δ13C–εNd cross-plots (45). The glaciation sequence shows that only after the growth of large continental ice sheets and a reorganization of both the global and Southern Ocean carbon budget was a weaker ocean-circulation regime established.

**Conclusions.** Comparison of proxies from a single core thus yields a temporal sequence of major climate events for the last glacial initiation and termination. During the last glaciation, climate and ice volume changed first, followed by the global carbon budget, which was in turn followed by ocean circulation. During deglaciation, the global carbon budget changed before ocean circulation strengthened. These temporal sequences show that thermohaline circulation changes did not trigger ice-sheet changes and global carbon budget reorganization. During the glaciation, strong ocean circulation and marine conditions in the North Atlantic likely provided an important source of moisture for continental ice-sheet growth during the sustained cold conditions associated with the Northern Hemisphere insolation minimum at ~72 ky B.P. During interstadials through the last ice age, on the other hand, simultaneous changes in benthic δ13C and Nd isotope ratios allow for the possibility of an ocean-circulation trigger for these millennial interstadial warmings. The observation that ice-sheet growth and global carbon cycle shifts precede ocean circulation changes at major glacial-interglacial boundaries shows that thermohaline circulation was a later amplifier but not the primary instigator of glacial-interglacial climate change.

**References and Notes**

11. The εNd = the deviation of the 143Nd/144Nd of a sample from the bulk Earth value of 0.512683 (46) in parts per 10,000. The high-atmosphere Nd isotope (142 to 150 atomic mass units) and their single oxidation state (±3) inhibit significant mass-dependent fractionation. Moreover, corrections applied during mass-spectrometry measurement eliminate effects of any natural mass-dependent fractionation.
21. The Sr isotopes and rare-earth-element patterns of leaches from this core match that of seawater, which is evidence for a marine rather than detrital origin for the Nd isotopes.
40. If the Nd isotope ratio of the North Atlantic end member decreased and the Pacific end member remained constant at the time of the major δ13C change during the glaciation, it would be possible to buffer the Nd isotope ratio of South Atlantic deep water despite a weakening of thermohaline circulation. For example, the εNd of NADW would have to shift from εNd = −14 to −18 in concert with the MIS 5a/4 δ13C change (Fig. 1) and then rapidly shift back to −14 when we observe the change in the Nd isotope ratios. A complementary abrupt shift from ~10 and then another shift back to −14 could explain the apparent δ13C lead during the deglaciation. Although such scenarios, and variations thereof, cannot be completely ruled out, they require coincidental end-member εNd and δ13C shifts in both magnitude and timing such that the εNd (with nADW at the core sites remain roughly constant. Thus, they would require evidence before they can be considered seriously. On the longer term, as explained in the text, there is good evidence that the Pacific end member remained nearly constant on glacial-interglacial time scales, whereas the North Atlantic end member is less well constrained, but current evidence indicates near constancy (15, 18).
Very high energy (VHE) γ-rays probe the long-standing mystery of the origin of cosmic rays. Produced in the interactions of accelerated particles in astrophysical objects, they can be used to image cosmic particle accelerators. A first sensitive survey of the inner part of the Milky Way with the High Energy Stereoscopic System (H.E.S.S.) reveals a population of eight previously unknown firmly detected sources of very high energy γ-rays. At least two have no known radio or x-ray counterpart and may be representative of a new class of “dark” nucleonic cosmic ray sources.

Very high energy (VHE) γ-rays with energies $E > 10^{18}$ eV are probes of the nonthermal universe, providing access to energies far greater than those that can be produced in accelerators on Earth. The acceleration of electrons or nuclei in astrophysical sources leads inevitably to the production of γ-rays by the decay of $π^0$ produced in hadronic interactions, inverse Compton scattering of high-energy electrons on background radiation fields, or the nonthermal bremsstrahlung of energetic electrons. Several classes of objects in the Galaxy are suspected or known particle accelerators: pulsars and their pulsar wind...