The cubic phase Ic can be formed by condensation of donor as well as a double acceptor. In each case, the lattice consists of two-state structure which is stabilized by an infinite two-dimensional sheets are stacked on one another, and are interconnected by the formation of each oxygen atom is situated at the centre of a tetrahedral arrangement of its four

Although the pronounced intensification of Northern Hemisphere glaciation between 3.1 and 2.5 million years ago substantially lagged the full development of North Atlantic Deep Water formation, we propose that the increased atmospheric moisture content was a necessary precondition for ice-sheet growth, which was then triggered by the incremental changes in the Earth’s orbital obliquity.

The gradual closing of the Isthmus of Panama lasted from 13 to 1.9 Myr ago and 3–5 (all originally published ages were adjusted to the new astronomically dated timescale). Most evidence for restricted water-mass exchange through the Panama strait is based on sediment records from Caribbean and Pacific Deep Sea Drilling Program (DSDP) sites 502 and 503. Significant changes in planktonic foraminiferal assemblages occur at 6.8, 4.6, 2.5 and 1.9 Myr (ref. 4). A surface-water salinity increase in the Caribbean at 4.6 Myr is indicated by δ18O values of planktonic foraminifera^1 and implies a shoaling of the seaway to <100 m water depth. Shallow-water fossils from both sides of the Panama–Costa Rica region indicate^2 that the closure was almost complete at 3.6 Myr, but the final closure allowing land mammal exchange was achieved^3 at 2.7 Myr, coincident with the glacial-induced sea-level drop during the main intensification of Northern Hemisphere ice-sheet growth. However, the identification of the particular step in the closure of the Panamanian gateway that acted as a critical threshold for profound changes in deep-ocean circulation and climate remained qualitative and speculative^4. Here we present proxy data which demonstrate that the closure has affected deep ocean circulation since 4.6 Myr ago.

Today, a mixture of nutrient-enriched, low-δ13C Antarctic Intermediate Water (AAIW) and nutrient-depleted, high-δ13C Upper North Atlantic Deep Water (UNADW) and Mediterranean Overflow Water cross the Atlantic-Caribbean sills at 1,600–1,900 m (Windward Passage, Anegada-Jungfern Passage) and fill the deep Caribbean basins. During the past 2.5 Myr, the relative proportion of northern- and southern-component water masses were related to glacial–interglacial differences in the formation rate of UNADW^5. A weaker UNADW formation during interglacials led AAIW to extend further north and result in a less ventilated, more corrosive Caribbean deep water. Hence, the Caribbean Sea is a highly sensitive recorder of ventilation changes in the upper Atlantic if the sill depth remained constant. Tectonic evidence from the Lesser Antilles arc and Aves ridge suggests no significant vertical movements since the middle Miocene (20–15 Myr ago) when a thick crust was established; vertical movements of <100 m Myr^−1 are expected, which were likely to have been closer to a few metres per Myr (ref. 11).

We report epibenthic foraminiferal δ18O, δ13C and percentage sand records of the carbonate fraction from ODP Site 999 (12°44’N, 78°44’W, Colombian basin, water depth 2,828 m) for the time interval 2.0–5.3 Myr. The δ13C values of Cibicidoides wuellerstorfi are a proxy for deep-water ventilation^6, as δ13C of sea water is closely linked to seawater nutrient and oxygen levels, with higher δ13C values indicating lower nutrient concentrations and better ventilation^7. The sand content (>63 μm) of deep-sea carbonates is a sensitive indicator of changes in carbonate dissolution. The sand content (foraminifera shells) decreases as dissolution progresses^8. The δ18O of C. wuellerstorfi is a proxy for changes in continental ice volume and deep water temperature. The age model of Site 999 is based on δ18O stratigraphy, and was correlated to the astronomically dated δ18O records from equatorial east Pacific Site 846 (ref. 6) and equatorial east Atlantic Site 659 (ref. 15).

Oceanographic conditions that result in changes in both δ13C and sand contents are documented in Figs 1 and 2. Before 4.6 Myr, low epibenthic δ13C values and low sand contents indicate a poorly ventilated deep Caribbean and severe carbonate dissolution. In the early Pliocene, similar low δ13C values of ~0.2‰ have been
documented only at subantarctic South Atlantic Site 704 (ref. 16) (2,532 m water depth), in contrast to higher North Atlantic values of ~1‰ (for example, sites 659, 552 (ref. 17)). This suggests that the Caribbean deep water was dominated by a δ13C-depleted Southern Ocean water mass (AAIW) before 4.6 Myr. After 4.6 Myr, deep-water ventilation as well as carbonate preservation increased into the late Pliocene due to a deepening of the lysocline. This is interpreted to reflect a progressively stronger influence of less corrosive and δ13C-enriched northern component water due to an increase in UNADW formation. This increase at 4.6 Myr is paralleled by an increased formation of Lower North Atlantic Deep Water (LNADW) as indicated by records of deep-water ventilation (Fig. 1) and carbonate preservation in the equatorial east (ODP sites 659 and 665 (ref. 18)) and west Atlantic (Ceará rise depth transect, sites 925–929 (ref. 19)) below 3,000 m water depth.

A first ventilation maximum in the Caribbean Sea as well as in the deep Atlantic was reached at 3.6 Myr, when Caribbean δ13C values approached those from North Atlantic component water (Site 659, Fig. 1). This mechanism supplied additional heat and moisture to the Northern Hemisphere and may have contributed to the mid-Pliocene warmth. Since 3.6 Myr, both sites 999 and 659 show similar isotope records of sites 999 and 846 demonstrates a substantial change in the Northern Hemisphere and may have contributed to the mid-Pliocene warmth. Since 3.6 Myr, both sites 999 and 659 show similar 18O records between 3.1 and 2.5 Myr (Fig. 3) and by the massive appearance of ice-raftered debris in northern high-latitude oceans since 2.7 Myr (ref. 25). The intensification of Northern Hemisphere glaciation finalizes the Cenozoic cooling trend, which started in the early Eocene and is marked by first indications of ice sheets in Antarctica 36 Myr ago. This long-term cooling is considered to be a direct response to permanent removal of atmospheric CO2 through enhanced silicate weathering and/or enhanced burial of organic carbon resulting from tectonically uplifted areas such as the Himalayas and American West. This long-term cooling brought the climate system of the Earth to a state critical for ice-sheet build-up in the Northern Hemisphere. This has been the case since ~10–5 Myr ago, when the first, and minor, occurrence of ice-raftered debris in the Arctic and North Atlantic indicates the first attempts of the climate system to start a glaciation. However, until 2.7 Myr ago, the climate system failed to amplify and continue a large Northern Hemisphere glaciation.

To initiate and continue the build-up of the prominent Laurentide and Scandinavian ice sheets, three factors are needed to act together. First, general cooling must have reached a critical threshold to allow precipitation to fall as snow rather than rain. Second, moisture needs to be introduced to high northern latitudes. Our results suggest that moisture was provided by an increased thermohaline circulation and Gulf Stream flow since 4.6 Myr, well before the intensification of Northern Hemisphere glaciation. Third, astronomical theory requires that the summer in northern high latitudes must be cold enough to prevent winter snow from melting. High-amplitude fluctuations in the Earth's obliquity (low tilt angle) triggered cold summers in the Northern Hemisphere, and prepared the way for strengthening of the glacial-interglacial 41-kyr cycles during late Pliocene and early Pleistocene. However, a pronounced long-term minimum in obliquity amplitude fluctuations occurred between 4.5 and 3.1 Myr (ref. 31). The δ18O records of sites 659 (ref. 15), 846 (ref. 6) and 999 show that during this unfavourable orbital configuration there may have been several failed attempts of the climate system to start the glaciation, for example during 4.1–3.9 Myr and 3.5–3.3 Myr. We therefore suggest that the progressive increase in obliquity amplitudes between 3.1 and 2.5 Myr was the final trigger for amplification and continuation of the long-term expansion of Northern Hemisphere ice sheets after the necessary preconditions were met 4.6–3.6 Myr ago by formation of the Isthmus of Panama. These incremental changes in obliquity, coupled with changes in the background state of the ocean, suggest a threshold value for ice-sheet growth, which should be testable with climate models.

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Our data provide a precise picture of the final phase of NADW intensification that had been developing during the mid-Miocene. In response to the gradual emergence of the Central American seaway, we observe an enhanced thermohaline overturn since 4.6 Myr that reached a first maximum at 3.6 Myr. This was amplified by an increased salt transport to the North Atlantic and the initiation or intensification of UNADW formation in the Labrador Sea, as predicted by recent results from global circulation model simulations. In support of this interpretation, we note that results from the Labrador Sea (ODP Leg 105) indicate increased bottom-water currents and drift sedimentation since ~4.5 Myr (ref. 24).

The closure of the Panamanian seaway has always been an attractive candidate for the ultimate cause of the Pliocene intensification of the Northern Hemisphere glaciation. The pronounced ice-sheet growth in Eurasia, Greenland and North America is marked by a progressive δ18O-enrichment in benthic foraminifera δ18O records between 3.1 and 2.5 Myr (Fig. 3) and by the massive appearance of ice-raftered debris in northern high-latitude oceans since 2.7 Myr (ref. 25). The intensification of Northern Hemisphere glaciation finalizes the Cenozoic cooling trend, which started in the early Eocene and is marked by first indications of ice sheets in Antarctica 36 Myr ago. This long-term cooling is considered to be a direct response to permanent removal of atmospheric CO2 through enhanced silicate weathering and/or enhanced burial of organic carbon resulting from tectonically uplifted areas such as the Himalayas and American West. This long-term cooling brought the climate system of the Earth to a state critical for ice-sheet build-up in the Northern Hemisphere. This has been the case since ~10–5 Myr ago, when the first, and minor, occurrence of ice-raftered debris in the Arctic and North Atlantic indicates the first attempts of the climate system to start a glaciation. However, until 2.7 Myr ago, the climate system failed to amplify and continue a large Northern Hemisphere glaciation.

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According to the theory of plate tectonics, rocks found in the vicinity of mid-ocean ridges—where oceanic plates are created—should be relatively young (at most several Myr old). Here we report the discovery of zircons with ages of about 330 and 1,600 Myr that were drilled from exposed gabbros beneath the Mid-Atlantic Ridge near the Kane fracture zone1–4. Age determinations were made using the $^{207}$Pb/$^{206}$Pb evaporation method$^{5}$ and confirmed with conventional U–Pb dating and ion microprobe (SHRIMP) analysis. We suggest two plausible explanations for the origin of these unusually old zircons. During the opening of the Atlantic, sheared crustal material or delaminated continental lithosphere sank into small roll-like circulation cells$^{6}$ that developed in the shallow mantle at each side of the ridge axis and the material was then transported through these cells to the ridge axis. Alternatively, material from the continental crust has been trapped within the Kane fracture zone since the opening of the Atlantic Ocean basin through a series of transform migrations and ridge jumps$^{7}$, with portions of this material subsequently migrating down the ridge axis.

Leg 153 of the Ocean Drilling Program drilled five sites on the western valley wall of the Mid-Atlantic Ridge (MAR) between 23°20′N and 23°30′N, 5–35 km south of the Kane transform (Fig. 1). This area is located in the central Atlantic Ocean, ~2,000 km from the continental margins and far from any islands. Leg 153 recovered harzburgites of the upper mantle which were depleted by partial melting followed by the formation of gabbroic melts$^{8}$. The peridotite–harzburgite–gabbro complex is interpreted to be uplifted and exhumed by normal faults$^{9}$,10. The gabbros comprise normal gabbro, olivine gabbro, gabbro-norite, olivine gabbro-norite, olivine norite, and troctolite.

From the recovered cores, we selected 30 gabbro samples from material drilled 7.7–68.9 m below the sea floor. These samples were the least altered ones and did not contain visible schlieren and veins. While performing oxygen-isotope investigations of these gabbro samples, we discovered numerous zircons. Some of these samples contain 1–4 zircons in 5 cm$^3$; however, close to 40 zircons were found in sample 137. The number of zircons identified does not correspond to the Zr content of the host rock (mean ~20 p.p.m.). The morphology of zircons in samples from the same borehole is similar, but differs in samples from different boreholes. Most of the zircons are 20–60 μm in size, yellow-white and transparent with some reddish tear-type inclusions, and sometimes show a lineation parallel to crystal faces (Fig. 2). Frequent types in the Pupin diagram$^{11}$ are P1, P2, G1 and G2, with short prismatic shapes being most abundant. Sample 122 from borehole 922A contained zircons that were of irregular, or had no discernible, shape. Zircons in gabbro complexes which occur mainly in veinlets and schlieren have been reported several times$^{12,13}$. In thin sections of these zircons are seen at the borders between mineral grains; in one case, a zircon was included in an ilmenite grain$^{14}$. However, our sampling avoided visible veins, schlieren and any signs of alteration as far as possible, but those used for our age determinations are clearly different from those which may be formed in the highly differentiated rest-magma of the gabbroic melts.

If the zircons were formed during the generation of the gabbro magma, then their age would be expected to be ~1 Myr (ref. 1); because of their U contents it would be difficult to determine a U–Pb age. To reveal the history of these zircons, we first made $^{207}$Pb/$^{206}$Pb age determinations of carefully selected single zircons from three samples (samples 134 and 137, borehole 923A; sample 122, borehole 922A), using the well established mass-spectrometric evaporation method$^{5}$. All zircons contain both radiogenic lead and small, but significant,