hydrogen bonds per water molecule, with each molecule acting as a double
acceptor as well as a double donor. In each case, the lattice consists of two-
dimensional layers of hexagonal rings in the chair conformation. These puckered
sheets are stacked on one another, and are interconnected by the formation of
hexagonal rings composed of three molecules each form adjacent layers. The
two forms of ice I differ only in the stacking sequence of the puckered layers
relative to one another, such that the interconnecting rings are in the boat
conformation in ice Ih, while they assume the chair conformation in ice Ic.

techniques has afforded a relatively clear understanding of the structure of
water in the solid state, and 12 polymorphic forms of ice, denoted as I0, Ic
and II–XI, have been characterized to date. Phases I0 and Ic are the two most common forms of ice and are
strikingly similar in structure (Fig. 4). Extended water aggregates are
also encountered in multi-component crystals and well-known examples include biological macromolecules15 and clathrate hydrates16. We also note that a recent study has produced a solid-state
structure which is stabilized by an infinite two-dimensional
sheets are stacked on one another, and are interconnected by the formation of
hexagonal rings composed of three molecules each form adjacent layers. The
two forms of ice I differ only in the stacking sequence of the puckered layers
relative to one another, such that the interconnecting rings are in the boat
conformation in ice Ih, while they assume the chair conformation in ice Ic.

An improved understanding of the three-dimensional structural aspects of water has important implications in the area of structural biology. Indeed, investigations of the forces at play in macromolecular interactions19 have demonstrated the importance of water structuring, and this point has been illustrated by several examples including the structures of *Scapharca* dimeric haemoglobin19, crambin20, actinidin11 and carbonic anhydrase C (ref. 22). There is much evidence that alludes to the presence of ordered water clusters in the active clefts of these proteins, but unambiguous positional information is still rare. It is thought that water molecules contribute to the complex stability by mediating hydrogen bonds between the functional groups of the protein and the ligands, and by filling potential voids or holes inside the binding site23.

The structure reported here demonstrates that the ice Ic arrangement can be a favourable conformation for a water cluster in a mixed-component system, even at room temperature. It also shows how the cluster and its surroundings assume a complementary relationship, resulting in the void available to the cluster being optimally occupied both in terms of packing efficiency and the maximization of intermolecular interactions.

**Figure 4** The structures of the ice phases I0 (a) and Ic (b). Oxygen atoms are shown as circles and hydrogen bonds are represented as lines. The darkened portions depict the smallest representative structural motif in each case. The hexagonal phase Ic is formed when water is cooled below its freezing point at atmospheric pressure. The cubic phase I0 can be formed by condensation of water vapour below −80 °C, or via a phase transition from vitreous ice or ices II, III or V. Above −80 °C, ice Ic itself transforms irreversibly to ice Ih. In both instances, each oxygen atom is situated at the centre of a tetrahedral arrangement of its four nearest-neighbour molecules. Its hydrogen atoms and lone pairs of electrons are directed towards these neighbours, thus facilitating the formation of four hydrogen bonds per water molecule, with each molecule acting as a double

The Late Cenozoic closure of the seaway between the North and South American continents is thought to have caused extensive changes in ocean circulation and Northern Hemisphere climate2–3. But the timing and consequences of the emergence of the Isthmus of Panama, which closed the seaway, remain controversial4. Here we present stable-isotope and carbonate sand fraction records from Caribbean sediments which, when compared to Atlantic and Pacific paleoceanographic records, indicate that the closure caused a marked reorganization of ocean circulation starting 4.6 million years ago. Shallowing of the seaway intensified the Gulf Stream and introduced warm and saline water masses to high northern latitudes. These changes strengthened deep-water formation in the Labrador Sea over the next million years—as indicated by an increased deep-water ventilation and carbonate preservation in the Caribbean Sea—and favoured early Pliocene warming of the Northern Hemisphere. The evaporative cooling of surface waters during North Atlantic Deep Water formation would have introduced moisture to the Northern Hemisphere.

Acknowledgements. We thank C. Barnes for assistance with the unit cell and space group determination. This work was supported by the US NSF.

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**Effect of the formation of the Isthmus of Panama on Atlantic Ocean thermohaline circulation**

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Received 5 February, accepted 6 April 1998.

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**Supplementary information** is available on Nature's World-Wide Web site (http://www.nature.com) or as paper copy from the London editorial office of Nature.

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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 (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 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 that the closure was almost complete at 3.6 Myr, but the final closure allowing land mammal exchange was achieved 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. 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. 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 Antilanes 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, 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. 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. 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 δ13C maxima and reflect the increased strength of northern component water masses. During cooler periods, δ18O minima at Site 659 are more pronounced than those from Caribbean Site 999 and reflect vertical fluctuations of the LNADW-AABW mixing zone (AABW, Antarctic Bottom Water). Thus, even though LNADW may have been in the `reduced' mode during harsh climate episodes, the Caribbean was still relatively nutrient-poor compared to the deep Atlantic (Site 659) because of increased formation of UNADW. This suggests that the familiar dipole in the Pleistocene ocean circulation10,20 has been operating at least since 3.6 Myr ago.

The comparison between the Caribbean and Pacific sand-fraction records of sites 999 and 846 demonstrates a substantial change in ocean carbonate preservation at 4.6 Myr (Fig. 2). Before 4.6 Myr, vigorous carbonate dissolution characterized both the Caribbean and the Pacific. Beginning at 4.6 Myr, the increasing thermohaline circulation amplified the inter-basin fractionation between the Atlantic and Pacific, which is reflected in a strong increase in UNADW formation has been predicted by ocean model studies21.

Our data provide a precise picture of the final phase of NADW intensification that had been developing during the mid-Miocene22. 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 results23 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 glaciation2. The pronounced ice-sheet growth in Eurasia, Greenland and North America is marked by a progressive 18O-enrichment in benthic foraminifera δ18O records between 3.1 and 2.5 Myr (Fig. 3) and by the massive appearance of ice-rafted 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 late Pliocene and is marked by first indications of ice sheets in Antarctica 36 Myr ago25. This long-term cooling is considered to be a direct response to permanent removal of atmospheric CO2 through enhanced silicate weathering26 and/or enhanced burial of organic carbon27 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 buildup in the Northern Hemisphere. This has been the case since ~10–5 Myr ago, when the first, and minor, occurrence of ice-rafted debris in the Arctic and North Atlantic indicates the first attempts of the climate system to start a glaciation28. However, until 2.7 Myr ago, the climate system failed to amplify and continue a large Northern Hemisphere glaciation.

To initiate and continue the buildup 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 melting29. 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 Pleistocene14,30. 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 obliquity32, 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.


Figure 3 Calculated obliquity amplitude fluctuations20 and the benthic oxygen isotope record of Site 659 (eq. east Atlantic) versus age for the past 6 Myr. The arrows mark the Pliocene cooling trend between 3.1 and 2.5 Myr which resulted in the first large ice-sheet build-up in the Northern Hemisphere during interglacial stages G6–G6 (labelled).

Received 28 July 1997; accepted 14 April 1998.
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 zone. 

- The oldest gabbros were drilled from the Ontong Java Plateau, 4,150 km from the mid-ocean ridge, and are estimated to be between 330 and 200 Myr old. These gabbros are compositionally similar to the 500–250 Myr old gabbros in the Ontong Java Plateau, suggesting a similar origin.

- The younger gabbro samples were collected from the Pupin seamount chain, 2,000 km from the continental margins and far from any islands. These gabbros are estimated to be between 100 and 50 Myr old. Both age determinations are based on SHRIMP U-Pb geochronology.

These results challenge the conventional understanding of the evolution of the Pacific Ocean basin and provide new insights into the history of plate tectonics and the formation of oceanic crust.