Quaternary Deepwater Paleoceanography

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During the past decade, geochemical paleoceanographers have begun to explore the changes in the circulation of the deep ocean that occurred during the glacial-interglacial cycles of the earth's recent history. The deep ocean was significantly colder during the glacial maximum. The distributions of biologically utilized elements (such as carbon and phosphorus) were significantly different as well; higher concentrations of these elements occurred in the deep (>2500 meters depth) North Atlantic, and lower concentrations occurred in the upper (<2500 meters depth) waters of the North Atlantic and possibly in all of the major ocean basins. In contrast, relatively subtle changes have been observed in the radiocarbon ages of deep waters. Slow deepwater changes are statistically linked to variations in the earth's orbit, but rapid changes in deepwater circulation also have occurred. Deepwater chemistry and circulation changes may control the variability in atmospheric CO_2 levels that have been documented from studies of air bubbles in polar ice cores.

THE CIRCULATION AND CHEMISTRY OF THE DEEP OCEAN play major roles in maintenance of the earth's climate and must be understood in order to assess and to predict climate change. Deep currents moderate heat and water balances, and the chemical composition of the ocean (as modified by biological transport) regulates atmospheric CO_2. Modern ocean and ocean-atmosphere models are sophisticated in their construction, but they still do not account for all relevant physical and chemical aspects of present climate. Also, models are constructed to mimic the behavior of the modern climate; therefore, their sensitivity to perturbations from modern conditions may be incorrect. In order to improve model sensitivity and in order to gain some model-independent understanding of processes and possible configurations of the ocean-atmosphere system, it is helpful to examine climate with respect to the widest range of boundary conditions. Deep-ocean sediments contain one of the most complete and extensive records of climate history, including climate transitions that compare in magnitude with typical "doubled atmospheric CO_2" scenarios. The ocean climate record is sufficiently detailed to allow examination of the sensitivity of climate to one well-known forcing, the variation in the geographic distribution of incoming radiation due to variations in the earth's orbital parameters. Finally, some ocean sediments have sufficient temporal resolution to allow examination of climate changes on the critical time scale of a few decades.

Most knowledge of past oceanic conditions concerns the ocean surface, because it is based for the most part on the sedimentary record provided by fossils of organisms that dwell near the surface (*1*). Although studies of these fossils by CLIMAP and successor investigations have been enormously successful, these results do not tell us much about what is occurring at deeper levels in the ocean. During the past decade, investigations of geochemical properties of benthic foraminifera have provided a window into past behavior of the deep ocean. These studies are not as extensive as those of ocean-surface organisms, but they have shown that significant alterations have occurred in ocean circulation and chemical distribution patterns.

Interest in deepwater paleoceanography also derives from ice core bubble observations showing that atmospheric CO_2 during interglacial times was ~280 ppmv but was less than ~200 ppmv during glacial times (*2*). This change must have been driven by the oceanic carbon system. The ocean is the only C reservoir sufficiently massive yet temporally responsive enough to account for a change of this magnitude. A series of models have illustrated that there are several ways in which oceanic circulation, chemistry, and biological activity can alter atmospheric CO_2 levels (*3, 4*), but there is no general agreement as to which (if any) of these mechanisms is dominant. Many of these uncertainties could be removed if appropriately detailed data on deep ocean chemistry and circulation were available. It is beyond the scope of this article to review all of the factors that might control glacial-interglacial cycles in the partial pressure of CO_2 in the atmosphere, but some hypotheses attribute glacial atmospheric CO_2 cycles entirely to oceanic circulation and chemical distributions; hence, these can be investigated by paleodeepwater studies.

Deepwater Circulation Problems

Although scientists who study the physical circulation of the contemporary ocean might emphasize how little is still known, certain basic features of deep ocean circulation are reasonably well understood. Deepwater circulation is largely thermohaline (the density of seawater is determined by temperature and salinity), meaning that water must be sufficiently dense to sink into the deep ocean, where flows are driven by the density gradients created by these sinking deep waters as governed by the laws of fluid dynamics on a rotating sphere. Cooling of course is common at high latitudes, but in many cases (in particular, the North Pacific), water is insufficiently salty to become dense enough to sink to the bottom of the ocean even when cooled to the freezing point. Therefore, in addition to the obvious densification provided by severe winter cooling, the earth's hydrological balance plays a significant role in determining where deep water can form. Deep water forms in surprisingly few parts of the ocean: North Atlantic Deep Water (NADW) is known to form in the Greenland, Norwegian, and Labrador seas by intense cooling of sufficiently salty source waters.

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Antarctic Bottom Water (AABW) is known to form in the Weddell and Ross seas, where cooling is reinforced by increased salinity through ice freezing. Dense bottom water is also formed in the Mediterranean and Red seas, where evaporation from these basins increases salinity. These dense waters are considerably warmer than those formed from polar sources. They flow over restricted sills and mix with less dense waters and sink only to intermediate depths of the ocean. Intermediate water formation also occurs in the North Atlantic, Antarctic, and North Pacific oceans. The deep water of the ocean derives from these limited source areas, which represent only a small part of the total area of the ocean.

Upon leaving their source regions these water masses flow away from their sources and interleave and admix with the other deepwater sources. At present, AABW is denser than NADW, so this water mass occupies the deepest parts of basins where topographic barriers do not prevent its entrance. In addition to having distinct dynamically active properties such as temperature and salinity, these water masses start off with distinct chemical signatures, which are modified by chemical reactions along their flow path. Hence water masses can be traced usefully through their chemical properties.

Major concerns about deepwater circulation are focused on the limited number of sources and their potentially extreme sensitivity to small perturbations; it might not be that hard to shut off some sources or create new ones in the face of dramatic climate changes such as those associated with glaciation or those that might be associated with doubled atmospheric CO_2 levels. The driving forces could be thermal or hydrological (and both of these could be influenced by subsequent redistribution by ocean currents). And, of course, even if none of the extreme "on" or "off" scenarios occurs, major shifts in the relative production rates of the various water masses are possible.

The Paleoceanographer's Deepwater Strategy

Sedimentary particles in bottom deposits originate from near the surface (planktonic organisms and windblown minerals) or on the bottom (benthic organisms and authigenic precipitates); therefore, there is no direct window into the interior of the water column overlying a site. Instead, it is necessary to rely on the relative horizontal homogeneity of the ocean: waters that lap up onto the flanks of the mid-ocean ridge are generally not very different in physical or chemical properties from the waters in the interior of the basin at the same depth. Deepwater paleoceanographers thus aim to reconstruct bathymetric gradients of deepwater properties on the boundaries of basins; some horizontal resolution is possible by examination of opposite boundaries of a basin. In addition, some marginal basins are rapidly filled by waters above a specific sill depth and are not significantly modified within, so that sediments from a marginal basin, such as the Caribbean, offer the opportunity to sample external waters at the sill depth level from cores at any depth in the basin (as long as continued rapid ventilation and lack of modification can be proven).

Early Deepwater Work: Benthic Faunal Abundances and Non-geochemical Tracers

Initially it was hoped that investigation of deep ocean properties could follow the lead set by the studies of planktonic fossils in which faunal abundances were used to infer near-surface conditions. Relative population abundances of benthic foraminiferal species vary throughout the modern ocean, and they also vary in deep-ocean sediment cores on glacial-interglacial time scales (*5*). As data accumulated, however, it proved difficult to assign the relative species population differences to specific water properties such as temperature or dissolved oxygen (O_2). In small regions (for example, on the scale of a single basin) reasonable correlations between the relative benthic faunal population abundances and water properties were often observed, but these correlations broke down on larger scales (interbasin and interocean). Indeed, one indication of the elusiveness of benthic foraminifera as tracers of water properties is provided by the use of the term "Uvigerina water" (*6, 7*) to indicate a faith that surely something in the water controls the abundance of the benthic genus *Uvigerina*. But it may transpire instead that factors unrelated to the deepwater properties may have significant roles in controlling relative population abundance, such as the type and abundance of planktonic food from the surface or the depositional environment. In any event, it is fair to assert that benthic foraminifera have so far defied a systematic generalization of factors controlling their species composition.

A number of non-geochemical indicators of deepwater flow have been investigated. The study of advective tracers relies on the occurrence of unique source areas of particular particles; for example, diatoms that grow only in Antarctic waters. When these tracers are found at some distance from their source, one can infer that a current has brought them to the new site and thereby a direction of transport (*8*). One problem with these advective tracers is that they do not readily provide quantitative information on fluxes or velocities, but rather simply whether a flow did or did not occur or semiquantitative information at best. It is not always clear that sources are sufficiently localized to provide definitive information, and there is some ambiguity about where in the water column the advective transport occurs. Nonetheless, in some cases these advective tracers are quite useful; when Antarctic diatoms are found in deep ocean sediments at 35°S, it is clear that AABW has been flowing to the north—at least some of the time (*8*).

Sediment texture indicators have also been examined to some extent; for example, variations in the grain size of sediments have been used to infer the intensity of bottom flow (*9*). The anisotropy of sediment properties has also been suggested as an indicator of flow direction (*10*). As with the advective tracers, however, it is difficult to relate the grain size variations to specific quantitative paleoenvironmental parameters.

Geochemical Indicators of Past Deepwater Properties

Benthic foraminifera encapsulate records of some of the geochemical properties of the bottom waters overlying the sediments. These properties are the oxygen isotope ratio (*11*), which is a function of the oxygen isotope composition of the water and the deepwater temperature; the carbon isotopic ratio (*12*), which for some species appears to reflect the carbon isotopic composition of bottom water; the cadmium (Cd) and barium (Ba) contained in solid solution in the calcium carbonate crystal lattices, which reflects the Cd and Ba contents of the bottom water; and the ^{14}C age of benthic foraminiferal shells, which can be compared to the ^{14}C age of coexisting planktonic shells to give a measure of the ventilation age of the bottom water. Although these properties in modern benthic shells would not have been the obvious choice of a chemical or physical oceanographer trying to reconstruct modern ocean circulation and chemistry, they are useful for paleoceanographic reconstructions because: (i) they can be linked quantitatively to specific properties of the deep water; hence, they can be used to test ocean circulation models quantitatively; and (ii) the distribution of some of these tracers in the modern ocean is analogous to other tracers that we generally do wish to know; for example, the oceanic Cd distribution is similar to the phosphorus (P) distribution, which influences patterns of oceanic productivity and the cycling of CO_2 in the ocean.

Of these tracers, all except benthic ^{14}C ages give information only on the patterns of deep ocean circulation and do not (except perhaps indirectly and imprecisely) contain any information about the rates of ocean circulation. In some cases, however, pattern indicators may give information about relative rates; for example, the flux of NADW relative to that of AABW. Conversely, benthic ^{14}C ages give information both about relative patterns and absolute rates. All of these tracers (as well as their counterparts in the modern ocean) give model-dependent results; that is, the result must be interpreted through some conceptual or quantitative model, and at any level of data detail, it is probable that there will be more than one model capable of accounting for the data. Despite this problem (common to inverse problems), both pattern and rate tracers are extremely useful in examining the circulation of the ocean now and in the past. Although geochemical tracers may not be able to specify a unique solution for ocean circulation patterns, they can quite effectively rule out some models that otherwise might have been considered.

Oxygen isotopic composition and deepwater temperatures. The $\delta^{18}O$ studies have been of great importance in establishing the glacial-interglacial stratigraphy of oceanic sediment cores (*13*). This utility arises because global ice volume controls mean oceanic $\delta^{18}O$ and hence also the $\delta^{18}O$ of foraminifera, where about two-thirds of the Quaternary signal is due to seawater $\delta^{18}O$ variability. Until recently, less use has been made of the residual one-third of the fossil carbonate $\delta^{18}O$ variation, which is attributable to temperature, because the magnitude of the ice-volume signal was uncertain. Recent studies of past shorelines have clarified this situation, because sea level changes are dominated by changes in global ice volume. The most important developments have been (i) establishment of concordant sea level curves based on high stands of sea level from coral terraces on three rising oceanic islands (Barbados, New Guinea, and Haiti) (*14*), and (ii) establishment of a nearly continuous sea level history for the past 18,000 years from submerged coral samples drilled from the flank of Barbados (*15*). This knowledge allows estimation of the residual $\delta^{18}O$ signal due to temperature. A mean oceanic $\delta^{18}O$ curve can be constructed from these sea level curves once a mean $\delta^{18}O$ for glacial ice is assumed. At face value, comparison of this curve with the benthic $\delta^{18}O$ record for the past 150,000 years indicates that average deep ocean temperatures were similar to those of the modern ocean only during the highest stands of sea level (oxygen isotope stages 1 and 5e, which correspond to the last 10,000 years and about 125,000 to 115,000 years ago, respectively); at all other times the deep sea was about 2°C cooler than at present (*16*). The rate of change of the transitions between these two states is still being worked out, but it seems to follow the pace of deglaciation or glacial onset. This major cooling of the deep ocean has yet to be explained.

Although receiving less attention so far, it is also possible to use $\delta^{18}O$ variations to reconstruct variations in the thermal structure of the ocean. Limited evidence from the U.S. continental margin indicates that the glacial thermocline temperature gradient was similar to that of the modern ocean (*17*); however, detailed data may alter this picture somewhat.

One uncertainty in these deepwater paleotemperature reconstructions is the role of regional isotopic variability (which is usually correlated with salinity variations) in modifying the temperature signal (*18*). At present there is no direct way to unravel the relative role of isotopic variability in water masses from local temperature variability, and attempts to establish past salinity variations have relied on indirect deduction and argument. Most workers suspect that the temperature variability is the larger part of most deepwater records, but this is not to say that the role of water isotopic variability of deep waters is negligible.

While many paleoceanographers feel comfortable with the apparent resolution in recent years of the relations among benthic $\delta^{18}O$, sea level, and deep sea temperature changes and the evidence of apparent glacial cooling of the deep ocean, some climatologists have expressed reservations about how such a large cooling could have occurred [for example, (*19*)]. A refined time history of these changes is needed, as is independent verification. Lehman (*20*) has suggested that amino acid epimerization in radiocarbon-dated shells may provide critical data for understanding past deep-ocean temperatures.

Deepwater $\delta^{13}C$ and Cd. The distribution of the $^{13}C/^{12}C$ ratios and Cd in the modern ocean reflect the biological cycling of organic matter as modified by circulation patterns (*21*). Organisms preferentially take up ^{12}C relative to ^{13}C (by 2%); hence, ocean surface waters are left with higher $\delta^{13}C$. Oceanic biota also efficiently take up essential elements such as P and N (henceforward referred to as "nutrients") from surface waters. For reasons that are somewhat less well understood, they also take up dissolved Cd efficiently as well; therefore, nutrient-depleted open-ocean surface waters contain low concentrations of Cd (*22*). The biological debris that sinks out of the surface layer decays almost quantitatively (~99%), and most of this decay occurs in the upper 1 to 2 km of the ocean (*23*). Hence, deep waters are lower in $\delta^{13}C$ and O_2, and higher in P, N, and Cd than surface waters. Because water masses such as NADW and AABW derive from waters of different history and accumulate different amounts of decaying debris along their flow path, water masses can be traced from the $\delta^{13}C$ and Cd signatures. Combination of a physical circulation model with a parameterization for biological uptake, sinking, and decay allows use of $\delta^{13}C$ and Cd data to obtain a model-dependent picture of circulation flow patterns of the ocean. In this respect, the distributions of $\delta^{13}C$ and Cd are similar to those of O_2 and P, which are more commonly applied as indicators of water masses in the modern ocean. Deepwater nutrient concentrations in the modern ocean increase from Atlantic to the Antarctic to the Pacific oceans (*24*).

Because benthic foraminifera incorporate deepwater C into their shells, the $\delta^{13}C$ distribution in past oceans can be determined. Application of this method is complicated in that benthic foraminifera are not in thermodynamic equilibrium with C isotopes in the water; various species have significantly different offsets from the $\delta^{13}C$ of the water (*25*), and some species apparently can have variable offsets (*26*). Zahn *et al.* (*26*) have suggested that some of these offsets could result from infaunal habitats (sedimentary pore waters have more negative $\delta^{13}C$ because of organic decomposition), although this habitat preference is only hypothetical and has never been demonstrated for the key indicator fossils used for deepwater $\delta^{13}C$ studies. Furthermore, at face value this hypothesis seems contradicted by Cd and Ba evidence, because these tracers do not show differences among species with large $\delta^{13}C$ offsets (*27, 28*). Even though Cd and $\delta^{13}C$ respond to somewhat different processes in pore waters, these tracers are all offset from bottom water composition in the oxic porewaters where benthic foraminifera would be viable. In any event, species that live at depth in the sediment would not be suited for paleo–bottom water studies, because pore water $\delta^{13}C$, Cd, and Ba compositions will be significantly different from those in the water column (*29*). Current practice is to use preferred species that appear to record the bottom water composition most reliably. Whatever the origin of variable offsets among different species, their presence led to erroneous conclusions in early studies of benthic $\delta^{13}C$. Studies that did not report which species were used or did not establish reliability of the signal by use of preferred species should not be relied upon. A second complication in the $\delta^{13}C$ paleodeepwater technique arises because mean oceanic $\delta^{13}C$ is not constant through time; C with low $^{13}C/^{12}C$ from organic matter currently on the continents is transferred into the ocean during glacial times; the most recent estimates for this shift place the global mean $\delta^{13}C$ of 18,000 years ago at −0.3 to −0.5 per mil relative to that of the present ocean (*30*). As for the $\delta^{18}O$ temperature technique, a relation for variations in mean oceanic $\delta^{13}C$ must be constructed in order to use this paleotracer. In practice, this correction has often been achieved by construction of a common chronology for sediment cores and then calculation of the difference in $\delta^{13}C$ between them. Sedimentary processes and imperfections in the chronology will transmit errors into the difference signal, so that only difference data from the best cores or the largest amplitude signals from typical cores should be considered reliable.

Foraminifera also substitute Cd for Ca in the crystal lattices of their $CaCO_3$ shells, and the composition of cleaned benthic foraminifera shells reflects that of the Cd content of the bottom water (*27*). Unlike $\delta^{13}C$, Cd does not show major offsets between several major species and genera, so that it is not necessary to restrict comparisons to data from a single species or to apply species correction factors. Oceanic mean Cd does not vary much between glacial and interglacial times, so that it is not necessary to apply a correction to time series data. The lack of species offsets and global mean variability makes downcore benthic Cd easier to interpret as a record of changing nutrient concentrations of bottom water. On the other hand, foraminiferal Cd is more difficult to measure than $\delta^{13}C$, and fewer laboratories are capable of making these measurements; thus fewer data are available.

Where both tracers are reliably recording bottom water compositions, and proper allowance is made for ocean-continent carbon transfer and sedimentary artifacts, such as time-scale miscorrelations and bioturbation, foraminiferal $\delta^{13}C$ and Cd should give similar information about deep ocean circulation patterns. When the two methods agree, some confidence can be placed in the nutrient-proxy interpretation of the data. When the two methods disagree, one or both may be wrong, presumably because bottomwater properties are not being accurately represented or because some aspect of their geochemical cycle has not been considered (*31*).

In the North Atlantic Ocean, Cd and $\delta^{13}C$ data are generally concordant. Both tracers indicate that mid-depth (~3000 m) waters in the North Atlantic had higher nutrient contents during glacial times than at present, but also that this increase is not so high as to eliminate the difference between the Atantic and Pacific oceans (see Fig. 1) (*32, 33*). Recent $\delta^{13}C$ evidence has shown that this situation prevailed during most of the past 2.5 million years (*34*). Both tracers also show that the nutrient contents of the upper waters (~700 m to 2500 m) were lower than those of the modern North Atlantic, as well as those at depth in the glacial North Atlantic. In general, this evidence implies that the deepest waters of the glacial Atlantic received lesser proportions of nutrient-poor NADW than that today and that the NADW was partly replaced by water from nutrient-rich sources.

Even though $\delta^{13}C$ and Cd data for the glacial North Atlantic are in accord, more than one circulation interpretation is still possible. The most common variants, as implied above, are that the flow of NADW was reduced and flow of some North Atlantic nutrient-depleted intermediate water was enhanced. Alternatively, nutrient depletions in the upper waters might be reduced if instead the source waters of the Antarctic Intermediate Water became depleted in nutrients rather than enriched. The actual mechanisms might be identified by improving the geographical coverage of the data (for example, if the presence of nutrient-depleted Antarctic waters could be demonstrated rather than surmised). Better control on variations in surface water characteristics in potential deepwater source areas is needed in particular. Some information of this type is available (*35*), but it is fragmentary and incomplete. Even a relatively complete knowledge of surface boundary conditions and the internal tracer distributions would leave room for interpretation, because any tracer will have multiple potential solutions at some level of desired detail. On the other hand, by the use of different types of tracers with contrasting boundary conditions, the range of possible solutions can be narrowed considerably.

Duplessy *et al.* and Kallel *et al.*, on the basis of $\delta^{13}C$ values from the upper waters of the Pacific and northern Indian oceans, suggested that the upper waters in these oceans (above 2500 m) were depleted in nutrients during glacial times compared to the levels occurring there today (*32, 36*). The available Cd data from these same cores support this notion, but the level of documentation is not as extensive as for the North Atlantic.

The most significant major disagreement between $\delta^{13}C$ and Cd data is in the South Atlantic and Antarctic region. The $\delta^{13}C$ data indicates that the deepest waters in this region were substantially enriched in nutrients during glacial times; yet, the Cd data indicates that there were no systematic differences in the nutrient status of these waters from glacial to interglacial times (*32, 33*). Whether this contradiction indicates that one (or both) of the tracers is wrong or that some special process that fractionates the tracers was operating is not known. Any interpretation of the nutrient content of Antarctic deep waters should be regarded with reservations until this apparent discrepancy is resolved.

Deepwater Ba. The distribution of Ba in the oceans is remotely similar to that of nutrients in that it is more abundant at depth than at the surface because of biological cycling but is significantly different from that of $\delta^{13}C$ or Cd in that (i) Ba is never depleted to extremely low concentrations at the surface (the lowest surface water concentrations are about one-fifth of those in Pacific deep water), and (ii) Ba concentrations are usually higher in the deepest waters, resembling the distributions of Si and alkalinity more than that of P or N (*37*). These differences most likely are caused by less efficient biological removal of Ba from surface waters than for C and Cd and less efficient recycling in the upper waters of the ocean: most or all of the Ba recycling occurs on the sea floor. Ba is also incorporated in place of Ca into the $CaCO_3$ crystal lattice of benthic foraminiferal shells in proportion to its concentration in bottom waters. Cleaned foraminifera shells therefore can be used to investigate the distribution of Ba in ancient oceans (*28*). There is considerably less information on this new tracer than for $\delta^{13}C$ and Cd, but the major features are (*38*): (i) As for $\delta^{13}C$ and Cd, glacial Ba concentrations were also lower in the upper waters (<2500 m) of the North Atlantic Ocean than they are at present, and (ii) unlike for $\delta^{13}C$ and Cd, Ba concentrations in deep waters of the glacial North Atlantic and Pacific oceans are the same (that is, in glacial times there were no interocean Ba gradients in the deep water). This difference is attributable to the different vertical recycling efficiencies of these tracers, but under just what range of conditions this situation can occur is not yet certain. Lea (*38*) suggested that more rapid vertical mixing of Atlantic surface and intermediate waters could produce this result and illustrated the concept with a six-box model. Perhaps other ways will be found as well. In any event, this difference between Ba and labile nutrient tracers illustrates why it is useful to have more than a single type of deepwater tracer to examine deepwater circulation. Some simple models that could account for major features of the $\delta^{13}C$ and Cd data would be inconsistent with Ba deepwater uniformity. For example, the North Atlantic deepwater Cd and $\delta^{13}C$ data can be explained as simply the result of a small reduction in NADW flow; the deepwater Ba data can be explained as the result of complete cessation of NADW, but this explanation contradicts the former. Some process other than NADW cessation must account for the deep Atlantic Ba enrichment; perhaps that process is enhanced glacial mixing between the intermediate and surface waters of the Atlantic Ocean as mentioned above.

Benthic-planktonic ^{14}C age differences. In the modern ocean, the $^{14}C/^{12}C$ ratio of deep waters is lower than that of surface waters because of radioactive decay of ^{14}C as surface waters subduct or diffuse into the deep ocean. In principle this difference allows for a model-dependent calculation of the rate of water movements, and thus this tracer has received considerable attention during the past 30 years [for example, see (*39*)]. The same information is available from sediments less than about 30,000 years old by measurement of the ^{14}C age difference between surface-dwelling and bottom-dwelling foraminifera. Dramatically improved ^{14}C detection limits provided by accelerator mass spectrometry (AMS) has allowed this method to provide useful results during the past 5 years. There are some significant problems that must be overcome, however. The ^{14}C age difference is more susceptible to sedimentological artifacts than other tracers, because it requires comparison of measurements on two different groups of organisms. Because these organisms may have different abundance patterns in time, benthic biological activity can stir together individuals that grew at different times and hence create misleading age differences between benthic and planktonic individuals in the mixed sample. The most reliable data will come from cores from sediments that had high accumulation rates and either very uniform planktonic and benthic faunal abundances or coincident sharp abundance maxima. The limited available data (*40*) indicate that the ^{14}C age of North Atlantic deep water decreased from about 650 years during the last glacial maximum to about 350 years today. In the Pacific, the ^{14}C age appears to have remained about the same or decreased slightly (a few hundred years) to its present value of 1600 years. The Atlantic data imply that a water mass in relatively recent contact with the atmosphere continued to fill the North Atlantic during glacial times, although there may have been some reduction in the total flux, and the ^{14}C evidence does not say where this water originated. Broecker (*41*) considered the possibility that this high ^{14}C water might have come from Antarctic surface water, although he pointed out that this process is inconsistent with the $\delta^{13}C$ and Cd evidence. The Pacific data indicate that the overall ventilation rate of the ocean varied remarkably little in the face of drastic changes in surface climate and in deepwater mass distributions. If additional data confirm these interpretations (and if ^{14}C data can be obtained that can constrain the origin of the waters, a difficult task) they will place a major constraint on models for the circulation of the ocean during ice ages.

The sedimentary artifacts that compromise these measurements must be overcome so that we can settle upon the ventilation history of the deep Pacific Ocean during the past 30,000 years. Although ^{14}C ventilation rate estimates will always be more limited in extent than the pattern indicators, it would be helpful to obtain better vertical resolution (at least to the extent of determining the ventilation rate of the glacial upper-ocean low-nutrient water relative to deeper waters) and extend coverage to the major basins of the world ocean.

Temporal histories of deepwater properties. Up to this point, the discussion has been phrased as if the ocean could exist in only two states: glacial or interglacial. In fact, the pattern is more complex. For example, during oxygen isotope stage 3 (about 24,000 to 62,000 years ago), global ice volume was about half of its level during the glacial maximum, yet the $\delta^{13}C$, Cd, and Ba paleochemical data all show that NADW chemistry was comparable to that of the present (*32, 33*). Clearly, the climate system does not exist in just two modes. What governs the relative timing and amplitude differences between ice volume, deepwater, and other climate parameters? A likely mechanism is variations in the earth's orbital parameters, which directly control the seasonal and latitudinal pattern of incoming solar radiation (insolation) at the top of the atmosphere and indirectly control key climate properties (*42*). The 23,000-year precession cycle (as amplitude modulated by the ~100,000-year eccentricity cycle) and the 41,000-year obliquity orbital cycles have distinct patterns of forcing between hemispheres, seasons, and high latitudes relative to low latitudes (*43*); therefore, regionally sensitive components of the global climate system will most likely respond differently to these forcing patterns. The obliquity cycle directly affects high latitudes the most and is a likely candidate for modulating deepwater sources. Although the precession cycle has greatest influence on midlatitude insolation, it could also affect deepwater production by preconditioning salinities through the hydrological cycle and also by affecting the northward transport of heat. Assessment of the relative influence of the orbital cycles on deepwater climate requires long time series that cover many orbital cycles, and thus this type of study is labor-intensive. Very little data relevant to this matter has been published. From the data available, the signature of orbital cycles can be recognized in the deepwater fluctuations, although the mechanisms whereby this link is effected are not well understood.

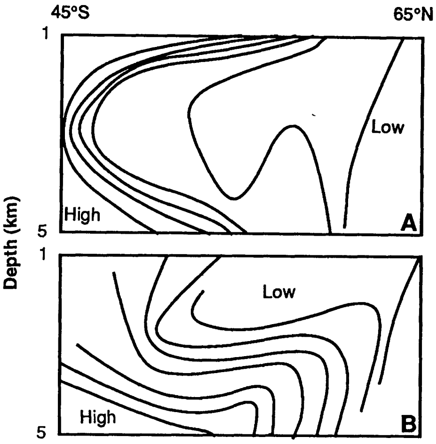

Fig. 1. Schematic illustration of the North-South P depth distributions in (**A**) the modern western Atlantic ocean [from GEOSECS data (*24*)] and (**B**) during the glacial maximum about 18,000 years ago [mainly from $\delta^{13}C$, but generally confirmed by Cd data (*32, 33*)]. Note that the top of each section is at 1 km depth not at the sea surface.

The degree to which the upper ocean and deep ocean chemical variations seen at the last glacial maximum are coupled or decoupled in time needs to be assessed. Do they march to the beat of the same drummer? Do orbital variations drive the deep ocean directly, or are deep ocean properties slaves to the surface climate? More long, detailed records of deepwater properties from the major basins of the world ocean are needed to answer these questions. More explicit documentation of the effect of sedimentary artifacts such as bioturbation on records should be developed. Although the existing deep-ocean time scale is good, there is no radiometric age control between 124,000 and 730,000 years ago. Radiometric constraints in this interval with a precision of 5000 years or less would test the orbital tuning hypothesis that the best present time scales are based upon (*44*). Single crystal $^{39}Ar/^{40}Ar$ dating of volcanic ejecta that can be linked to the deep ocean oxygen isotope record may be the key here.

Rapid Deepwater Changes

The potential rate at which climate change can occur is of particular concern to evaluation of our responses to potential climate-altering activities. If climate has sufficient resistance to rapid change, a strategy of adaptation might be viable. But if abrupt changes can occur, then a strategy of prevention might be preferred (if it is possible). The major concerns are on decadal to centuries

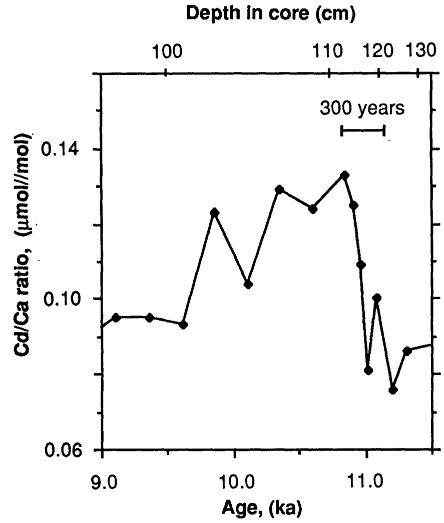

Fig. 2. Cd variability in the deep western North Atlantic during the Younger Dryas cooling event. Data are for *N. umbonifera* (*46*) with the AMS ^{14}C time scale derived from (*45*). The scale bar shows a 300-year interval. Because the actual rate of change is blurred by biological mixing of the sediment, the actual rate of change may have been significantly faster.

time scales, because this is the interval over which adaptation is difficult and changes might be irreversible. Although most deep ocean cores are not suitable for examining events of this duration (because the sedimentation rate is commonly only 2 to 5 cm per 1000 years or less), there are some unusual drift deposits (where fine-grained material is laterally focused toward a site) that have accumulated at rates up to 200 cm per thousand years (*45*). In particular, in one core with a moderately high accumulation rate (20 to 50 cm per 1000 years) from the deep western North Atlantic, Cd data show that deepwater chemistry can switch from a low-nutrient mode similar to that of the modern ocean to a higher-nutrient mode more similar to the glacial ocean in 300 years or less (*46*) (Fig. 2). On the basis of the chronology for this core, this switch occurred at the initiation of the Younger Dryas cooling event that punctuated surface temperatures in the far North Atlantic and Europe during the end of the last glaciation. These relations suggest that there is a possible genetic linkage between cold surface water temperatures in the North Atlantic and reduced NADW flow.

More evidence on deepwater fluctuations from higher accumulation rate sections of the North Atlantic Ocean and elsewhere will be crucial in establishing how rapidly ocean circulation can change. The chronology of deepwater fluctuations should be better integrated with those of potential forcing factors such as surface temperature and salinity.

Physical Modeling and Data-Model Intercomparisons

Relatively little paleodeepwater modeling of the physical circulation has been undertaken so far. One reason is that modelers are not completely satisfied with their current models and want to improve them before devoting computer time to paleosimulations. Coupled atmosphere-ocean models typically tend to run away from the modern NADW circulation and can only be brought into agreement with the observations by ad-hoc adjustments. One example is the study of Manabe and Stouffer (*47*) (Fig. 3), where an arbitrary readjustment of the surface freshwater balance was added to allow NADW to form. With initial conditions comparable to the modern ocean, and with the freshwater balance adjustment, their model simulated a deep circulation comparable to that of the present. But when the simulation was started in a configuration with low surface salinities in the North Atlantic, the model remained in this configuration even with the same freshwater balance adjustment as in the former case; this result shows that the model North Atlantic circulation has two stable self-sustaining modes. Similarly, another model study (*48*) showed that relatively small adjustments to the salinity of the surface waters of the model North Atlantic could rapidly set off similar mode transitions. It remains to be determined whether the real ocean is as sensitive to the freshwater balance as these models are, but the studies are intriguing because the two patterns that they produce resemble the observed glacial and interglacial circulation patterns.

As coupled ocean-atmosphere models improve, the sensitivity of the models to perturbations induced by ice sheet topography and orbital variations should be examined to determine the extent to which continuously variable or multiple restricted stable states exist and to determine the circumstances, by which transitions between states can be realized. We also need to understand to what extent the ocean climate system is deterministic (and predictable or chaotic) or stochastic.

Summary of Major Changes in Deep-Ocean Circulation

The major changes that are now evident in the character of the deep oceans between glacial and interglacial times are:

1) The deep ocean was about 2°C cooler during glacial times.

2) Nutrient concentrations were higher in the deeper waters (>2500 m) of the glacial North Atlantic than those today. This difference signifies that deep flow from nutrient-depleted source waters was less then. However, the evidence that deep Atlantic nutrient levels remained lower than those of the Pacific suggests that flow patterns were not reversed during glacial times.

3) Lower nutrient concentrations are indicated in the upper waters (1000 to 2500 m) of all oceans during glacial times; the most complete and convincing data is in the North Atlantic. This result signifies either that the relative flux of nutrient-depleted waters increased significantly to this depth interval or that the nutrient content of the source waters was significantly reduced.

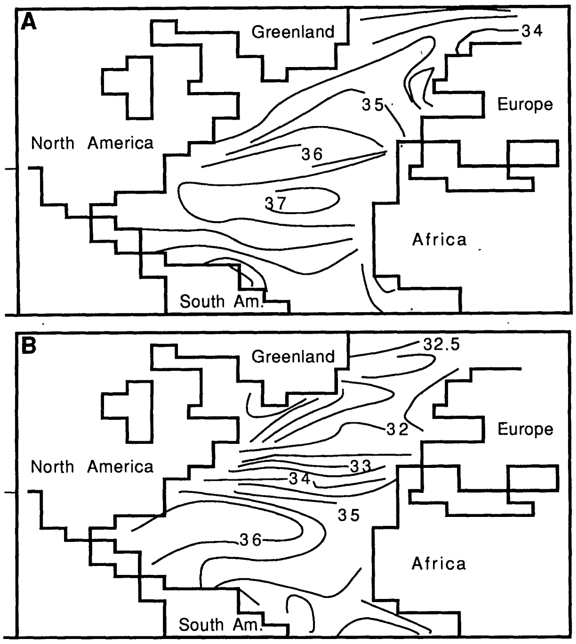

Fig. 3. Representation of the sea surface salinity distributions from the two circulation modes of a coupled ocean-atmosphere circulation model (*47*). Mode 1 (**A**) has a warm, saline high-latitude North Atlantic in which NADW formation occurs. Mode 2 (**B**) has a cold, fresh high-latitude North Atlantic in which NADW formation does not occur.

4) Unlike the labile nutrients, the concentration of Ba is similar in the North Atlantic and Pacific during glacial times. The exact cause of this difference is uncertain but must reflect the differential response of tracers that are regenerated in the upper ocean (Cd and $\delta^{13}C$) and on the sea floor (Ba).

5) The radiocarbon age of the North Atlantic decreased somewhat, from 650 years during glacial times to ~350 years today and the radiocarbon age of the Pacific decreased only slightly if at all, from about 2200 years to 1600 years today.

6) The deep North Atlantic circulation can change quite rapidly (300 years or less) from a pattern similar to the modern ocean to a pattern similar to that of the glacial ocean. This rate of change is nearly as fast as observed anywhere else in the global climate system.

Progress and Problems for the Future

Progress in the field of deepwater paleoceanography has been rapid during the past decade: the six conclusions above were not known (and in most cases, unsuspected) at the start of the decade. Most paleoceanographers would assign a high level of confidence to these conclusions, although the previous discussion indicates that there also are some significant contradictions between tracers. By now, the largest scale glacial-interglacial variations in chemical distributions have probably been uncovered, although the details of the distributions are sufficiently vague that we usually cannot trace water masses to their sources, and it is still possible to speculate about several different mechanisms that might change deepwater chemical distributions. The timing of these changes with respect to forcing factors such as the orbital insolation and with respect to other parts of global climate system remains vague, as do the potential causes of rapid deepwater transitions.

There is still very little data from large parts of the Pacific and Antarctic oceans, and spatial coverage of the upper ocean (500 to 2500 m) is adequate only for the North Atlantic and Northern Indian oceans. We need better control on surface water characteristics for $\delta^{13}C$, Cd, Ba, and ^{14}C in areas where deep water forms. Some information is available for $\delta^{13}C$ and Cd in planktonic foraminifera, but the reliability of this type of data is uncertain. Sufficient stratigraphic documentation (for example, at what depth in a particular core was the glacial datum taken? How good is the $\delta^{18}O$ curve? Which species was used?) should be provided in all studies.

With respect to the relation among ocean chemistry and circulation and atmospheric CO_2, the most important task is to clarify the uncertainties in the chemistry (Cd and $\delta^{13}C$) of Antarctic surface and deep water. Better chronological control is needed on the relative timing of atmospheric CO_2 variations with respect to changes in oceanic chemistry. Published chemical box models for deep water chemistry and circulation attempt to account for only a limited set of data, typically only one of the available tracers emphasized. More work needs to be done to incorporate all of the available constraints into the models so that the robustness of the solution can be assessed. It is necessary also to explain the timing of atmospheric CO_2 changes as well as the magnitude.

Some of the key properties that we use in the modern ocean to examine circulation and carbon chemistry are not available for the study of past oceans other than by indirect deduction or resolution of small differences between large numbers. One cannot say whether the following properties will ever have useful paleo-indicators, but they would rank high on the wish list of most paleoceanographers:

1) *Paleosalinity*. While $\delta^{18}O$ of foraminifera is in part determined by the isotopic composition of the water, and $\delta^{18}O$ of the water is correlated with salinity, this information is useful only in special circumstances (for example, glacial meltwater; in the vicinity of large river runoff; and perhaps in determining large regional sea-surface salinity differences). A paleosalinity indicator that was precise to at least 1 per mil would help confirm and clarify those cases where $\delta^{18}O$ has been used for this purpose in the past, and an indicator that was good to 0.1 per mil or better would have great utility.

2) *Paleo-dissolved* O_2. Surface waters can equilibrate with dissolved O_2 without equilibrating with $\delta^{13}C$ or losing Cd, so that O_2 concentrations cannot be ascertained confidently from those tracers. Because the O_2 content of the deep water can affect sediment geochemistry and benthic populations, a more direct estimation of dissolved O_2 is desirable.

3) *Paleoalkalinity or paleocarbonate saturation*. Large variations in the accumulation rates and seafloor dissolution of calcium carbonate have been known and explored semiquantitatively for some time, but we still don't have a quantitative indicator that is directly linked to the degree of saturation of the bottom water. A better tracer of deep water $[CO_3^{=}]$ would improve our understanding of variability of atmospheric CO_2.

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Seeing Phenomena in Flatland: Studies of Monolayers by Fluorescence Microscopy

CHARLES M. KNOBLER

Monolayers formed at the interface between air and water can be seen with fluorescence microscopy. This allows the phase behavior of these monolayers to be determined by direct observation and opens up the possibility of following the kinetics of phase transformations in two-dimensional systems. Some unexpected morphologies have been discovered that provide information about the nature of monolayer phases and have connections to pattern formation in other systems.

RESEARCHERS HAVE LONG BEEN INTRIGUED THAT BY ALMOST trivial means (*1*) one can produce a monolayer—a structure only a single molecule thick—at the interface between air and water. Monolayers formed by substances that are insoluble in the liquid subphase are called Langmuir monolayers. These are distinguished from Gibbs monolayers, which result from the preferential adsorption at an interface of substances that are soluble in the bulk, and Langmuir-Blodgett films, which are formed when Langmuir monolayers are transferred to solid substrates.

The amphiphilic molecules that form Langmuir monolayers have hydrophilic and hydrophobic portions, and it is the balance between these opposing natures that keeps the molecules at the surface. Long-chain fatty acids are typical monolayer-formers; their carboxyl head groups remain immersed in the water while their hydrocarbon tails limit their solubility. Chains longer than about 12 carbons are necessary to keep the solubility low but, if the hydrophobic character of the chain is dominant, the substance will form a lens rather than a monolayer on the surface.

Life scientists have investigated phospholipid Langmuir monolayers in order to gain insight into the structure and properties of bilayers, which serve as models for cell membranes. More recently, the resurgence of interest in complex fluid systems that are composed of amphiphiles (emulsions, microemulsions, and lamellar systems) has stimulated monolayer research. (It is interesting that much of what was once called colloid chemistry is now seen regularly in the condensed-matter sections of journals such as *Physical Review Letters*.)

The desire to investigate the effect of dimensionality on the equilibrium and dynamic properties of physical systems has also stimulated monolayer experiments. I began to study Langmuir monolayers in order to extend my research on the kinetics of phase transitions in fluid mixtures to two-dimensional systems. This goal has not yet been realized, in part because the experimental problems are more significant than I had realized, but mostly because we have been sidetracked by the discovery of a rich variety of unexpected phenomena. It is these phenomena that will be the focus of this article.

Phase Behavior of Langmuir Monolayers

One prepares Langmuir monolayers (*2, 3*) by depositing a solution of an amphiphile in a volatile solvent onto a clean water surface; the monolayer spreads spontaneously as the solvent evaporates. If the solubility of the amphiphile in the subphase is negligible, a monolayer can be thought of as a separate phase with thermodynamic properties analogous to those of three-dimensional (3-D) systems. The pressure p is replaced by a surface pressure π, and the volume V becomes the area A. A barrier can be moved across the surface of the water to change the area available to the

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