

morphogenesis of the diatom cell wall. A completely different type of protein, a member of the papain family of proteolytic enzymes, was recently shown to be associated with silica spicules of a marine sponge (23). This protein catalyzes in vitro hydrolysis of silicon ethoxides (24) and thus may be involved in releasing silicic acid from a putative precursor molecule in vivo. In contrast, silaffins are ideally adapted to promote silicic acid polycondensation and precipitation of biogenic silica. First, as pointed out by Iler (19), possible candidates for flocculating agents involved in silica precipitation are cationic polymers and hydrogen-bonding polymers. Exactly these structural elements are present in silaffins, which are polycationic molecules containing a high proportion of hydroxy-amino acids (predominantly serine) and are thus ideally suited for ionic and hydrogen-bonding interactions with the surface of silica particles. Second, silaffins are covalently modified by the oligo-*N*-methyl-propylamine unit that chemically resembles the polyamine structures found to catalyze silicic acid polymerization (25) and to promote silica flocculation (26). The modifications strongly increase the cationic charge of silaffins and were shown to be essential for silica formation at acidic pH values. Diatom SDVs have been shown to be acidic compartments (18), and therefore the polyamine structure is indispensable for silaffins to exert silica precipitation activity at the pH conditions within the SDV lumen. To our knowledge, the oligo-*N*-methyl-propylamine modification has not yet been found in any other biological system. Further analysis of the role of silaffins in nanofabrication of diatom cell walls might offer biomimetic approaches for the synthesis of siloxane-based materials.

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15. Purification of silaffin-1A. HF extract from *C. fusiformis* cell walls was prepared as described (12) and fractionated on a size-exclusion column (Superdex-PEptide HR-10/30, Amersham Pharmacia Biotech). Chromatography was performed in buffer A [250 mM NaCl, 20 mM Tris-HCl (pH 7.5)] at a flow rate of 250 μ l/min. Eluting material was recorded at 226 nm and fractions were analyzed by Tricine-SDS-PAGE (13) and Coomassie blue staining. Fractions containing pure silaffin-1A were pooled, dialyzed against H₂O, lyophilized, and dissolved in H₂O to a final protein concentration of 10 to 30 μ mol/ml.
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29. We thank G. Lehmann and E. Hochmuth for technical assistance; T. Maurer and H. R. Kalbitzer for NMR analysis; and F. Siedler and H. Sarioglou for MS/MS analysis. We are indebted to G. Wanner for field-emission SEM analysis and R. Wetherbee for help with TEM analysis. We gratefully acknowledge W. Tanner for critically reading the manuscript. This work was supported by the Deutsche Forschungsgemeinschaft (SFB 521).

21 July 1999; accepted 30 September 1999

A Possible 20th-Century Slowdown of Southern Ocean Deep Water Formation

Wallace S. Broecker,¹ Stewart Sutherland,¹ Tsung-Hung Peng²

Chlorofluorocarbon-11 inventories for the deep Southern Ocean appear to confirm physical oceanographic and geochemical studies in the Southern Ocean, which suggest that no more than 5×10^6 cubic meters per second of ventilated deep water is currently being produced. This result conflicts with conclusions based on the distributions of the carbon-14/carbon ratio and a quasi-conservative property, PO_4^* , in the deep sea, which seem to require an average of about 15×10^6 cubic meters per second of Southern Ocean deep ventilation over about the past 800 years. A major reduction in Southern Ocean deep water production during the 20th century (from high rates during the Little Ice Age) may explain this apparent discordance. If this is true, a seesawing of deep water production between the northern Atlantic and Southern oceans may lie at the heart of the 1500-year ice-rafter cycle.

Circulation changes in the upper ocean have been shown to be an integral part of El Niño cycles, but there has been relatively little discussion concerning the possibility that circulation changes in the deep sea have occurred during the course of the present century. The last well-documented major change in thermohaline circulation occurred in association with the Younger Dryas cold event that ended ~11,500 calendar years ago (1). Only at the

time of the so-called 8000-years-ago cooling event is there a suggestion of a weakening in the strength of the Atlantic's large-scale circulation during the present interglacial period (2). Rather, circulation is often thought of in terms of a smoothly operating Holocene conveyor (3). Now, tantalizing evidence suggests that the current rate of deep water formation in the Southern Ocean may be several times smaller than its average over the course of the last ocean mixing cycle (that is, ~800 years).

There is an apparent inconsistency between long-term ventilation rates based on the global distributions of PO_4^* and ^{14}C and those based on observations of the Weddell Sea over the past two decades (4). The distribution of PO_4^* [PO_4^*

¹Lamont-Doherty Earth Observatory of Columbia University, Palisades, NY 10964, USA. ²Ocean Chemistry Division, Atlantic Oceanographic and Meteorological Laboratory, National Oceanic and Atmospheric Administration, Miami, FL 33149–1026, USA.

$= \text{PO}_4 + (\text{O}_2/175) - 1.95 \mu\text{mol/kg}$] shows that the entire deep Pacific and Indian oceans are filled with a nearly uniform mixture of water with $\text{PO}_4^* = 1.38 \pm 0.05 \mu\text{mol/kg}$, intermediate between $\text{PO}_4^* = 0.73 \mu\text{mol/kg}$ for deep water formed in the northern Atlantic and $\text{PO}_4^* = 1.95 \mu\text{mol/kg}$ for recently ventilated dense water spilling off the margin of the Antarctic continent into the abyss of the Weddell and Ross seas. Because these northern and southern source waters are completely mixed during their passage around Antarctica, we conclude that nearly equal amounts of deep water originate in the northern Atlantic and around the perimeter of the Antarctic continent. Furthermore, in order to satisfy the deep sea's ^{14}C budget over the last ventilation (mixing) cycle, each of these sources must, on the average, have supplied ~ 15 sverdrups [$1 \text{ sverdrup} = 10^6 \text{ m}^3/\text{s}$] of ventilated water to the deep sea (4, 5). This conclusion has been verified by a box-model simulation (5). Yet, studies carried out in the Weddell Sea show that no more than 4 sverdrups of ventilated deep water are generated in this source region (4). This mismatch between observations reflecting the long- and short-term operations might result from temporal variability in the strength of the Southern Ocean source or from deep water being produced in sizable quantities at other locations around the perimeter of Antarctica. The resolution of this seeming inconsistency may lie in the deep sea chlorofluorocarbon (CFC) inventories (6).

The completion of the World Ocean Circulation Experiment (WOCE) program in the Southern Ocean has made adequate information available to permit the compilation of a reliable inventory of deep Southern Ocean CFCs. Only over the past few decades has newly ventilated deep water carried these tracers. Newly produced deep water in the Southern Ocean is saturated to $\sim 70\%$ with CFC-11 (Fig. 1). On the available time scale (a few decades), little of this tracer is returned to the surface. Furthermore, because of the high measurement sensitivity, little of this tracer has escaped detection as the result of dilution during its spread away from the source regions. On the basis of an integration of Southern Ocean CFC-11 (7), we conclude that, over the past several decades, ventilated bottom water (8) has formed at an average rate of 4 sverdrups. In contrast, CFC-11 inventories for the northern Atlantic yield a production rate of deep water broadly consistent with that required to balance the Atlantic's natural ^{14}C budget (9). Thus, the CFC inventories seem to rule out the hypothesis that other as yet unmapped source regions around the perimeter of the Antarctic continent are currently heavy contributors to deep water production. This finding suggests that ventilation of the deep Southern Ocean is episodic rather than steady.

Processes operating along the margins of the Weddell and Ross seas may be incapable of

supplying much more than 4 sverdrups of ventilated deep water. If so, then polynyas or open ocean convective cells must be responsible for the much higher past production of ventilated deep water. If such events have supplied an average of ~ 10 sverdrups of ventilated deep water at times in the past, their frequency must at that time have been far greater than during the past 25 years.

Although a range of scenarios could be envisioned to account for these observations, here we explore one that calls on much stronger Southern Ocean deep water formation during the Little Ice Age (~ 1350 to 1880 A.D.), a period of relatively cold climate in the region around the northern Atlantic that came after the so-called Medieval Warm Period.

Little is known about conditions outside of Europe during the early and middle phases of the Little Ice Age, but a much better global picture of conditions during its terminal phase is available (Fig. 2). Mountain glaciers in the Swiss Alps, the southern Andes, and the New Zealand Alps were far more extensive in the mid-1800s than they are today (10) or at any other time during the Holocene. Mountain snow lines descended ~ 100 m below their current positions (compared to ~ 350 m below their current positions during the Younger Dryas and 950 m below their current positions during the peak of the last glacial period). The Little Ice Age cold phase in mountainous areas came to an end during the latter part of the 19th century. By the beginning of the 20th century, mountain glaciers in temperate and tropical regions were in full retreat. This retreat has continued to the present. Further, as summarized in Fig. 1, the extensive sea ice coverage around Iceland during the 17th, 18th, and 19th centuries diminished rapidly during the early part of the 20th century.

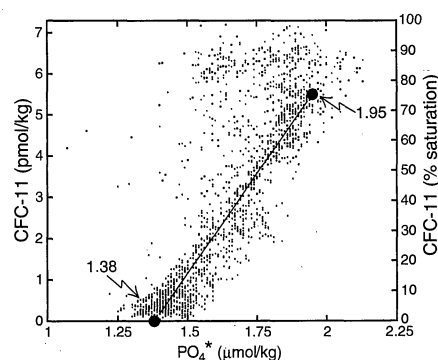


Fig. 1. CFC-11 concentration as a function of PO_4^* for waters south of 40°S from depths less than 500 m and with temperatures less than 3°C . Many of the points scatter around a mixing line joining the compositions of CFC-11 free water with a PO_4^* value of $1.38 \mu\text{mol/kg}$ (characteristic of upwelling circumpolar deep water) and water with a PO_4^* value of $1.95 \mu\text{mol/kg}$ (characteristic of newly forming deep water). Newly forming deep water is $\sim 75\%$ saturated with CFC-11.

During the Last Glacial Maximum (11) and the Younger Dryas (12), the pattern of the ocean's thermohaline circulation differed from today's, and it is tempting to postulate that it was different during the Little Ice Age as well. However, because the recent cold snap had a muted intensity (were such a change to have occurred during the Little Ice Age), it was likely different in character. In constructing a scenario in which the Southern Ocean ventilation was, on the average, much stronger in the past than it is currently, decisions regarding the timing of these changes must be made. If the Little Ice Age began during the 13th century (10, 13), then most of the last cycle of oceanic ventilation (14) occurred under Little Ice Age conditions, and the contribution made to the existing pattern of deep sea properties by ventilation during the preceding Medieval Warm Period can, perhaps, be disregarded. If so, then the critical issue is to define when the demise of Southern Ocean ventilation occurred. The post-Little Ice Age warming occurred in two major steps: one between 1880 and 1945 and the other from 1975 to the present (15). Because the ocean observations span the second of these steps, it is less likely that a change occurred during this interval. Hence, if a single transition time were to be chosen, then, most likely, it would lie in the interval from 1880 to 1945 . Of course, it is possible that the transition occurred gradually over the entire 20th century and is still in progress. In any case, the post-Little Ice Age period of Southern Ocean quiescence is unlikely to exceed 100 years in duration or about one-eighth of the ocean ventilation time (14).

The current Southern Ocean bottom water

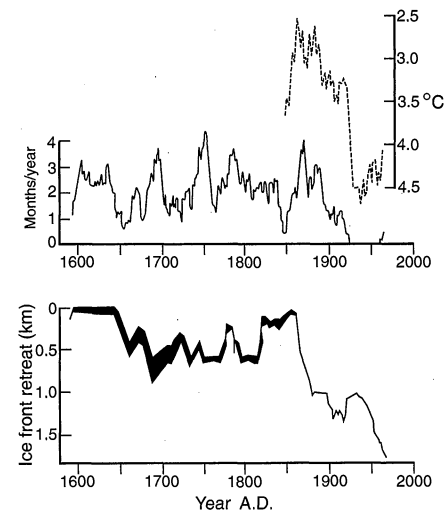


Fig. 2. Historic climate records dating to 1600 A.D. (**Top**) A record of the number of months per year that sea ice was present around Iceland (solid curve) and its relation to mean annual temperatures available since 1850 A.D. (dashed curve) (27). (**Bottom**) The extent of the front of the Grindelwald Glacier as reconstructed from oil paintings, drawings, prints, photographs, maps, and literature (28).

ventilation rate appears to be ~ 4 sverdrups. The constraint placed by PO_4^* and ^{14}C is that, on the average, the Southern Ocean and northern Atlantic contributions have been nearly equal and have totaled ~ 30 sverdrups over the course of the last ventilation cycle. Therefore, depending on the duration of the recent near shutdown, the rate during the Little Ice Age must have been correspondingly greater than 15 sverdrups. Of course, we would like to think that the production of deep water in the northern Atlantic was weaker during the Little Ice Age. However, the uncertainties in the ^{14}C -based estimate for the average ventilation rate over the past 200 years and in present-day ventilation rates (including the CFC-based estimate) are too large to lend support to such a conclusion.

During the interval of the last deglaciation, the temperature changes on the Antarctic polar cap were antiphased with respect to those on the rest of the planet (16–18). In particular, during the pronounced Bolling-Allerod warm interval, which brought to an end glacial conditions everywhere north of 45°S , the warming that had been underway in Antarctica during the previous 5000 years stalled. Only when the rest of the planet was plunged back into the cold Younger Dryas conditions did the warming in Antarctica resume. One explanation that has been proposed for this antiphasing is that an alternation between intense deep water formation in the northern Atlantic and in the Southern Ocean occurred (19, 20). Strong support for this idea comes from a reconstruction of the ^{14}C content of atmospheric and upper ocean C (1). This record requires a 5% rise in ^{14}C content of these reservoirs during the first two centuries of

the Younger Dryas. Only a conveyor shutdown provides a reasonable explanation for this rise (1, 19, 20). The climatic consequence of this bipolar seesaw could be a warming of Antarctica during the periods of intense deep water formation in the Southern Ocean and, of course, a cooling of the region around the northern Atlantic (19, 20).

This raises the question of whether the continent of Antarctica experienced warmer conditions during the Little Ice Age, when the region around the northern Atlantic was cooler and the extent of sea ice around Iceland was greater. The preliminary results of a deconvolution of the borehole temperature record obtained at Taylor Dome, Antarctica, suggests that temperatures were 3°C warmer during the Little Ice Age than they were during the Medieval Warm Period (21). If this preliminary conclusion withstands further scrutiny, then the pattern of global temperature change for the Little Ice Age would appear to be consistent with that for the Younger Dryas and, therefore, with greater deep water formation in the Southern Ocean at that time. At this point, a caveat is necessary; we do not understand how the change in deep ocean ventilation generated the observed magnitude of global temperature change (22).

One might ask whether such a dramatic change in deep ventilation created a pattern of deep ocean properties that might contradict the assumption that the deep sea is at steady state. The answer is that there is nothing about the present-day distribution of properties that is inconsistent with steady state ventilation. The question must then be asked in another way: Where in the distribution of these properties would one look for features that might point to

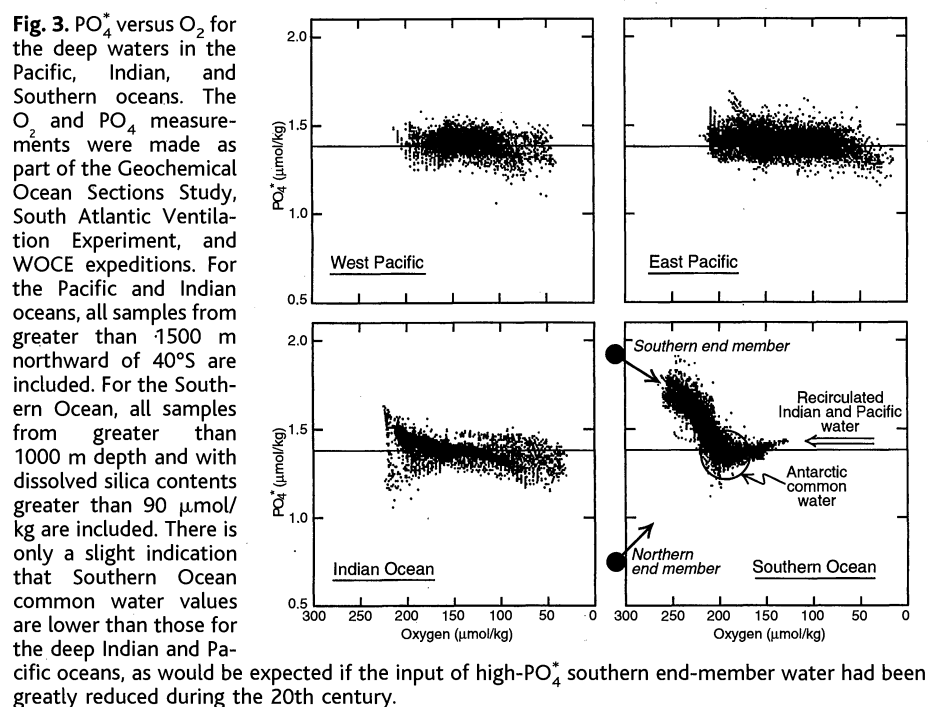
stronger Southern Ocean ventilation during the Little Ice Age? The most obvious place is the deep Southern Ocean. One would expect that the current dominance of northern component water would have reduced the PO_4^* for deep waters in the Southern Ocean below those for the interior of the deep Indian and Pacific oceans. Plots (Fig. 2) of PO_4^* versus dissolved O_2 (an index of the "age" of the water) show no discernible trend in PO_4^* in the deep Pacific or deep Indian oceans. Furthermore, there is only a slight indication that the PO_4^* in deep Southern Ocean water has decreased.

Using a 10-box ocean model, we have explored, in a preliminary way, the impact on the PO_4^* value for the deep Southern Ocean of a fourfold 100-year duration reduction in the rate of deep water formation in the south. As expected, the PO_4^* concentration of the deep Southern Ocean box undergoes a shift toward that for northern source water. After 100 years, the PO_4^* value for Southern Ocean deep water should have dropped by 12%. A reduction of this magnitude is not seen (Fig. 3). This may represent the shortcomings of the simple model, a flaw in our view of the data, or the failure of our hypothesis.

Our simple box model also suggests that a 100-year slowdown of Southern Ocean deep water formation would result in an increase of 14 per mil in the $^{14}\text{C}/\text{C}$ in atmospheric CO_2 (due to a backlogging in the upper ocean and atmosphere of newly produced ^{14}C atoms). Because the ^{14}C content of the atmosphere has been decreasing over the past 200 years, first as a result of the drop in ^{14}C production after the Maunder Minimum and then due to the input of ^{14}C -free CO_2 from fossil fuel production, it will take some effort to ascertain whether or not this predicted ^{14}C rise can be accommodated.

Two sources of evidence can be explored in hopes of obtaining a hint that a shift has indeed occurred. One is to contrast the results of temperature and salinity surveys made in the 1930s by the German oceanographic vessel *Meteor* to determine whether the northward penetrating wedge of colder and less salty bottom water in the western Atlantic AABW (Antarctic Bottom Water) has retreated during the past 60 years. This has yet to be done. The other is to study high-deposition-rate sediments for a ^{13}C and Cd change in benthic foraminifera shells formed during the Little Ice Age. Sediment in a core with a very high accumulation rate from near Bermuda shows a ^{13}C drop consistent with a greater extent of the AABW wedge during the Little Ice Age, but Cd measurements are at odds with this conclusion (23).

If the thermohaline hypothesis were to gain support, then the question will surely arise as to whether the Little Ice Age was a onetime event in the Holocene or whether it is part of a continuing cycle. Ice-rafting events in the northern Atlantic recur at ~ 1500 -year intervals (24, 25). No evidence exists for a substantial



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