molecular resonances \( \pi_1 \) and \( \pi_2 \), whose energies are \(-2.3 \) and \(-2.7 \) eV, respectively. These different threshold surface voltages indicate that the two \( S_1 \to T \) and \( S_1 \to S_2 \) movements are independent. Similarly, the observation that the \( S_1 \to S_2 \) motion is a one-electron process demonstrates that it is a direct process and not just a sequence of \( S_1 \to T \) and \( T \to S_2 \) motions. As seen in Fig. 2, the \( Y_{T \to S_1} \) yield for moving the molecule from the \( T \) to the \( S_1 \) state has an even lower threshold voltage than the \( Y_{S_1 \to S_2} \) and \( Y_{S_2 \to T} \) yield curves. This difference most probably originates because, when the STM tip is in position \( P_1 \) and activates the \( T \to S_1 \) movement, the molecule in the \( T \) transient state is no longer under the tip and the electronic excitation process must involve only the transfer of electronic excitations of the silicon substrate (24) to the molecule.

Direct evidence of the existence of the two \( \pi_1 \) and \( \pi_2 \) molecular resonances has been obtained by STM- \( I-V \) spectroscopy (Fig. 4 (25)). When mapping the \( I-V \) spectroscopy over the entire biphenyl molecule, a resonance at \(-2.1 \) eV (with slight variations of \( \pm 0.1 \) eV) was found localized over the mobile phenyl ring (Mo), and a second separate resonance at \(-2.5 \) eV (with slight variations of \( \pm 0.1 \) eV) was found localized over the fixed phenyl ring (Fi). This localization probably reflects the relatively weak coupling between the two phenyl groups of the molecule, which interact more strongly with the silicon surface. The slightly lower energies (0.2 eV) of the two \( \pi_1 \) and \( \pi_2 \) resonances observed in tunneling spectrosopy compared with their energies derived from the \( Y_{S_1 \to T} \) and \( Y_{S_1 \to S_2} \) yield thresholds result from the \( I-V \) spectroscopy method itself (25). The observed localization of the \( \pi_1 \) and \( \pi_2 \) resonances (Fig. 4E) correlates well with the localization of the corresponding \( S_1 \to T \) (\( \pi_1 \)) and \( S_1 \to S_2 \) (\( \pi_2 \)) yields. Indeed, the \( Y_{S_1 \to T} \) yield is much higher than the \( Y_{S_1 \to S_2} \) yield with the tip at position \( P_1 \) (Fig. 2). The \( Y_{S_1 \to S_2} \) yield has a maximum when the STM tip is at \( P_3 \) that rapidly decreased when the STM tip was moved away to positions \( P_1 \) and \( P_2 \). Thus, depending on the precise location of the STM tip inside the molecule, different electronically excited states (\( \pi_1 \) or \( \pi_2 \) resonances) of the molecular system can be produced, each associated with a specific molecular movement (\( S_1 \to T \) or \( S_1 \to S_2 \)).

Compared with other molecular quantum-control methods based on the use of photon absorption selection or coherent control rules (8), the real-space picoimeter-scale control method described here has the advantage of working with single molecules and of dealing with a completely different concept based on the selection of a specifically electronically excited state through the spatial localization of the excitation inside the molecule. This is a crucial step toward the development of a real quantum technology able to control the internal operation of future mono-molecular machines (26).

References and Notes
27. This work is supported by the European Research and Training Network AMMIST (contract HPRN-CT-2002-00299) and the European STREP NanoMan (contract NMP4-CT-2003-550660). M.M. also acknowledges support from a European Marie Curie fellowship (contract MEIF-CT-2003-502037). The authors thank G. Meyer for invaluable advice.

29 November 2004; accepted 23 March 2005

10.1126/science.1108048

Glacial/Interglacial Changes in Subarctic North Pacific Stratification

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Since the first evidence of low algal productivity during ice ages in the Antarctic Zone of the Southern Ocean was discovered, there has been debate as to whether it was associated with increased polar ocean stratification or with sea-ice cover, shortening the productive season. The sediment concentration of biogenic barium at Ocean Drilling Program site 882 indicates low algal productivity during ice ages in the Subarctic North Pacific as well. Site 882 is located southeast of the summer sea-ice extent even during glacial maxima, ruling out sea-ice–driven light limitation and supporting stratification as the explanation, with implications for the glacial cycles of atmospheric carbon dioxide concentration.

Air bubbles trapped in Antarctic ice reveal that the atmospheric concentration of carbon dioxide (CO\(_2\)) has varied over ice age cycles, between 280 parts per million by volume (ppmv) during interglacials (including the preindustrial Holocene) and 180 ppmv during peak glacial conditions (such as the last glacial maximum) (1). Because the ocean holds 50 times more inorganic carbon than does the atmosphere, the consensus is that changes in ocean/atmosphere exchange drove the CO\(_2\) changes, which in turn amplified climate forcings to yield the large observed amplitude of ice age cycles. However, the specific cause of glacial/interglacial CO\(_2\) change remains elusive.

CO\(_2\) is extracted from the atmosphere by phytoplankton growth in the sunlit surface ocean, and this carbon is then sequestered in the ocean interior by the downward rain of organic matter and its subsequent degradation back to CO\(_2\). This biologically driven sequestration of carbon in the ocean interior is referred to as the “biological pump.” In the modern ocean, the efficiency of the biological pump is limited by particular regions of the polar ocean: the Antarctic and the Subarctic North Pacific. In these regions, vertical exchange of water causes deep seawater to rise to the surface ocean via the outcrop of the Antarctic Bottom Water (AABW). To determine the origin of the low CO\(_2\) values observed in the Polar North Pacific, we present evidence for glacial/interglacial changes in the amount of AABW ventilation in the region.

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or decreased vertical exchange [polar ocean stratification (2)] would work to reduce this CO2 leak, both changes have been proposed to explain the reduction in atmospheric CO2 during the last ice age (3, 4).

Paleoceanographic data suggest that export production in the Antarctic Zone of the Southern Ocean was lower during glacial times (2, 5–7). This argues against increased polar ocean productivity as the driver of lower ice-age CO2 levels. However, these data do not necessarily rule out polar ocean changes as the cause of glacial/interglacial CO2 change. If the productivity decrease was driven by increased light limitation during glacial times because of nearly year-round ice coverage, then one would expect Antarctic surface partial pressure of CO2 to have been higher during glacial times. In this case, the region could not be taken as a driver of lower CO2 during glacial times unless sea-ice coverage was so pervasive as to prevent gas exchange between the surface ocean and atmosphere (8). In contrast, if this decrease in productivity was due to decreased vertical exchange, lowering the supply of nutrients from below (iron probably being the most critical), then the region may indeed have been a driver of lower glacial CO2, even without limitation of gas exchange by sea-ice coverage (2, 9).

Different paleoceanographic proxies of surface ocean nutrient status have yielded contradictory results and so have not yet convincingly distinguished between these two different scenarios for the observed glacial decrease in polar productivity (10). Although efforts are underway to understand paleoceanographic proxies through studies of the modern ocean, this ground-truthing has proven to be difficult. An alternative approach to distinguish among plausible interpretations of ambiguous paleoceanographic data is to take advantage of different coring sites to test the significance of down-core trends; this is the strategy followed here. We combine the measurement of biogenic barium (Ba), a paleoceanographic proxy of export production (11), with the use of the open Subarctic North Pacific as an analog to other polar sites (the Antarctic Zone of the Southern Ocean, the Sea of Okhotsk, and the Bering Sea) that differs substantially from these sites only in its history of sea-ice cover.

In sediments retrieved from Subarctic North Pacific Ocean Drilling Program (ODP) site 882 (Fig. 1) (50°21′N, 167°35′E, 3244 m water depth), we measured relative elemental concentrations at submillennial resolution, using the x-ray fluorescence (XRF) core-scanner at Bremen University, Bremen, Germany (12). Assuming that sedimentary aluminum (Al) or titanium (Ti) is exclusively of detrital origin, Ba abundance normalized to Al or Ti indicates the sedimentary concentration of biogenic (or excess) Ba (BioBa). According to the same reasoning, calcium (Ca) normalized to Al or Ti indicates the sedimentary concentration of biogenic calcium carbonate (CaCO3). The records of Al and Ti show almost identical trends and amplitudes, but the XRF signal is better for Al, which is thus used for normalization.

The BioBa record shows a strong climate-related signal (Figs. 2 and 3), with high concentrations during interglacials and lower values during cold stages. The large-scale Ba variations cannot be explained as the result of sulfate reduction and associated barite dissolution, because no significant sulfate reduction is observed in the interstitial water of late Pleistocene sediments of ODP site 882, and sedimentary organic carbon is uniformly low (13). Hence, the sedimentary Ba/Al or Ba/Ti ratio is interpreted to indicate lower BioBa accumulation and thus less export of organic matter from the surface ocean during cold periods, with the lowest BioBa concentrations coinciding almost exclusively with the glacial maxima. These data confirm previously reported observations from the Okhotsk Sea (14–16), the Subarctic Northwest Pacific (16, 17), and the Bering Sea (18) indicating that the export production in the Subarctic Pacific is similar to that of the Antarctic Zone of the Southern Ocean in its response to glacial/interglacial cycles.

However, as compared to the Antarctic or the Okhotsk Sea, the modern open western Subarctic Pacific near site 882 is characterized by much higher summertime sea surface temperatures (SSTs), reaching 12°C. SST reconstructions for the region from alkenones (19), foraminiferal Mg/Ca, and foraminiferal transfer functions (20) all indicate that, even during the coldest times, summertime SSTs never approached freezing. This corroborates evidence that ODP site 882 was located well east and south of the perennial sea-ice extent during glacial maxima (15, 21). As a result, sea-ice cover could not have been a major limitation on the spring/summer growing season during glacial times. Rather, the supply of nutrients must have provided the critical limitation on phytoplankton growth during glacial times. Iron appears to be the limiting nutrient today (22), although silicate may limit diatom production in some areas of the Subarctic Pacific during the late summer. The aeolian supply of iron to the region was, if anything, higher during colder times (23). Thus, the only clearly plausible mechanism for reducing the nutrient supply to the euphotic zone above site 882, regardless of which nutrient most constrained growth during the

Fig. 1. Global map of annual maximum sea-ice concentration. Black dots represent core sites from the Subarctic North Pacific and the Antarctic Zone of the Southern Ocean in which BioBa records have been measured [ODP 882; LV28-42-4 (15); MD84-552 (2); PS-1768 and PS-1772 (24); PS-1575, PS-1648, and PS-1821 (25); and PS-1565 and PS-2551 (26)]. The Antarctic sites, which occur over a wide range of latitude, and the record from the Okhotsk Sea show a similar correlation between productivity and climate as measured at North Pacific ODP site 882, with lower BioBa during ice ages. The colors indicate modern wintertime sea-ice extent (February and September for the Northern and Southern Hemispheres, respectively); the white dashed lines indicate modern annual minimum sea-ice extent (80% sea-ice concentration contour, based on satellite data from NASA International Satellite Land Surface Climatology Project Global Data Sets for Land Atmosphere Models). We used the http://ingrid.ldeo.columbia.edu/ Web site to design the map. The blue dot represents the Vostok ice-core site.
last ice age, is a reduction in the nutrient supply from below, as would result from polar stratification during cold periods. As described earlier, a similar correlation between productivity and climate appears to apply at various sites of different latitudes within the Antarctic, with lower BioBa accumulation during ice ages (2, 24–26) (Figs. 1 and 3). Given the constraint on the cause of the productivity drop in the open Subarctic Pacific, it follows that the same climate/productivity correlation in the Antarctic most likely arises from a parallel tendency for the Antarctic water column to stratify in cold climates (2, 9).

A strong temporal correlation exists between the Subarctic Northwest Pacific BioBa record and the D/H-derived temperature record from the Vostok ice core (1), applying not only to the major climate transitions but also to some of the more subtle climate variations (Figs. 2 and 3). Because the Subarctic Pacific itself is unlikely to have driven the climate changes observed in the Antarctic ice cores, Southern Hemisphere climate must modulate productivity (and, according to the logic above, stratification) in the polar North Pacific. Thus, we propose that deep water formation in the Antarctic during interglacials communicates Southern Hemisphere warming to the polar Northern Hemisphere, destratifying the Subarctic North Pacific, enhancing nutrient supply, and increasing productivity. The pervasive correlation between North Pacific stratification and Antarctic climate argues for a simple connection between polar ocean vertical stability and mean ocean temperature, such as is provided by the dependence of the thermal expansion coefficient of seawater on its absolute temperature (9).

The BioBa maxima during peak interglacials in isotope stages 1, 5, 7, 9, and 11 are accompanied by CaCO$_3$ maxima that contain up to 40% biogenic CaCO$_3$ in these otherwise carbonate-free sediments (Fig. 2). The near-absence of CaCO$_3$ in most of the record suggests that seafloor preservation of the CaCO$_3$ rain drives the bimodal character of the CaCO$_3$ record. Thus, we interpret the CaCO$_3$ peaks to indicate times of higher calcite saturation state in bottom water, although changes in the CaCO$_3$ flux may well have affected the peak amplitudes. If the CaCO$_3$ peaks were exclusively associated with deglaciation, they could be explained as the result of previously recognized processes not necessarily associated with the North Pacific (27). Specifically, at the end of ice ages, deeply sequestered CO$_2$ is released from the ocean back into the atmosphere, where it accumulates or is absorbed by the terrestrial biosphere. This causes a transient CaCO$_3$ preservation event in the deep sea that has been broadly observed (27). However, the fact that the CaCO$_3$ peaks persist through the interglacials indicates a glacial-to-interglacial increase in the calcite saturation state of the deep North Pacific. Because this saturation state change has not been so clearly observed in the lower-latitude Pacific (28), it is best explained as the result of oceanographic changes within the North Pacific region. Indeed, a higher deep ocean saturation state in the region would be the logical result of a weakening of the Subarctic North Pacific halocline, which would accelerate CO$_2$ escape through the North Pacific surface. This effect would have been magnified if interglacial weakening of the stratification was accompanied by less complete nutrient drawdown at the surface (10).

Although previously generated records of temperature- and salinity-related proxies in the North Pacific did not evoke an interpretation of enhanced glacial stratification, those records are not inconsistent with it. A reduction in the halocline during ice ages would have increased planktonic foraminiferal $\delta^{18}O$ by up to 1 per mil (%) more than dictated by glacial cooling and ice buildup. A sediment core raised near site 882 indicates a remarkably modest glacial-to-interglacial $\delta^{18}O$ decrease.
of \(\sim 1.1\%\) (20), \(\sim 0.8\%\) of which represents the global ice volume signal (29). Thus, there is very little room for glacial cooling, let alone a glacial increase in local surface salinity. Indeed, the strongest indication from extant planktonic foraminiferal \(\delta^{18}O\) data is that there was a gradual strengthening of the Subarctic Pacific halocline from the early Holocene to the present (30). Given other evidence of climate degradation since the early Holocene, we take this trend as further evidence of a cooling/stratification link. With improved age control for our site 882 BioBa record, we may be able to determine whether this same trend exists within earlier interglacial periods.

Modeling studies have yet to focus on the CO₂ impact of nutrient drawdown and/or stratification in the Subarctic North Pacific. The expectation is that the impact will be modest in comparison to similar changes in the Antarctic (31), which appears to ventilate much of the modern deep ocean (32). However, the evidence reported here for stratification in the Subarctic North Pacific during cold periods provides strong support for a similar change in the Antarctic, which has long been recognized as a potentially dominant driver of the glacial CO₂ cycles (3, 4, 33).

We noted previously that the Subarctic North Pacific underwent stratification upon the initiation of Northern Hemisphere glaciation 2.7 million years ago (34). Only later did it become clear that this was contemporaneous with similar stratification in the Antarctic (9). The bipolar nature of this phenomenon argued for a simple and general connection between climate and polar ocean vertical stability. Symmetrically, the data reported here indicate that the stratification during the late Pleistocene ice ages proposed previously for the Antarctic (2–4, 10) also occurred in the Subarctic North Pacific. This only strengthens our conviction that a simple physical mechanism must exist by which a cold climate leads to polar ocean stratification.

**References and Notes**
12. Materials and methods are available as supporting material on Science Online.
36. We thank R. Francois, M. Frank, and E. Galbraith for discussions and P. Rais (ETHZ) for technical assistance. P. Dulski and G. Schettler (GFZ Potsdam) provided the Inductively Coupled Plasma Mass Spectrometry (ICP-MS) and ICP–Optical Emission Spectroscopy calibration data, respectively. Financial support is provided by the Swiss National Science Foundation, the Deutsche Forschungsgemeinschaft, the U.S. NSF, and the Princeton University Carbon Mitigation Initiative sponsored by British Petroleum and the Ford Motor Company. This research used samples provided by the ODP. The ODP is sponsored by NSF and participating countries under the management of Joint Oceanographic Institutions.

**Supporting Online Material**
www.sciencemag.org/cgi/content/full/308/5724/1003/DC1

**Materials and Methods**
Reference
14 December 2004; accepted 24 March 2005
10.1126/science.1108696

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**Fig. 3.** Detail of Fig. 2, illustrating the strong correlation between the ODP 882 BioBa concentration (red, now plotted versus time) and the Vostok 8D record (gray) (7) over the past 150,000 years. To improve the correlation with the Vostok record, control points in the ODP site 882 age model have been adjusted from the initial age model (12). This model was based on foraminiferal \(\delta^{18}O\) data, which provide unambiguous markers of the glacial terminations but do not tightly constrain the age of mid-glacial–stage sediments (19). The adjustments to this model represent less than 5000 years in all cases. The BioBa record from Southern Atlantic site PS-1768 (24) is shown for comparison (blue; indicated in Fig. 1). The basic glacial/interglacial variations in the Subarctic Northwest Pacific and the Atlantic sector of the Southern Ocean, both in the sense of change and the absolute concentrations of sedimentary BioBa at minima and maxima. The age constraints for Antarctic cores are limited by a lack of preserved foraminifera, which is the likely reason for the poor temporal correlation at the detail level between ODP 882 and PS-1768-8.