tunneling is preferred for the shortest bridge length because of the large free-energy change between D and A. At longer distances, the poor scaling of direct tunneling favors a stepwise mechanism. Triplet energy transfer through π-stacked molecules is common in organic light-emitting diodes, and this intermediate regime between the strong distance dependence of tunneling and weak distance dependence of hopping may prove useful in understanding and designing energy transfer pathways in such devices.

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Subpolar Link to the Emergence of the Modern Equatorial Pacific Cold Tongue

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The cold upwelling "tongue" of the eastern equatorial Pacific is a central energetic feature of the ocean, dominating both the mean state and temporal variability of climate in the tropics and beyond. Recent evidence for the development of the modern cold tongue during the Pliocene-Pleistocene transition has been explained as the result of extratropical cooling that drove a shoaling of the thermocline. We have found that the sub-Antarctic and sub-Arctic regions underwent substantial cooling nearly synchronous to the cold tongue development, thereby providing support for this hypothesis. In addition, we show that sub-Antarctic climate changed in its response to Earth's orbital variations, from a subtropical to a subpolar pattern, as expected if cooling shrank the warm-water sphere of the ocean and thus contracted the subtropical gyres.

The equatorial Pacific cold tongue is a vivid expression of the ocean's thermocline, the contact between the pools of warm surface water circulating within the subtropical gyres and the colder ocean below. The trade winds drive an east-to-west downward tilt in the thermocline, which causes the thermocline to contact the ocean surface in the eastern Pacific, producing the cold tongue. An "El Niño" occurs when weaker trades allow the thermocline tilt to relax toward the horizontal, causing the cold tongue to disappear (*1*, *2*). The cold tongue is also sensitive to the mean depth of the thermocline (*3*), which can change on longer time scales, deepening in response to reduction in the meridional temperature gradient (*4*–*6*). If the thermocline deepens from its present position, the eastern cold tongue might eventually disappear.

Several authors have suggested that the warm-water volume was greater and the cold tongue absent in warm Pliocene times (*5*–*9*), with the cold tongue emerging only after adequate cooling had occurred. The existing paleotemperature data sets from the equatorial Pacific indicate that the emergence of the cold tongue during the Pliocene-Pleistocene transition was probably a multistage process that involved a different temporal behavior and signature at different locations and latitudes. The sea surface temperature (SST) reconstructions from the eastern part of the present-day cold tongue [Ocean Drilling Program (ODP) Site 846] seem to indicate that the latitudinal temperature gradient along the equator started to emerge around 4.3 million years ago (Ma) (*10*). However, the multiproxy paleotemperature estimates (based on alkenones and Mg/Ca paleothermometers) from a record located several hundred kilometers toward the west (ODP Site 847) show very little change at that time (*7*, *11*), indicating that the cold tongue, if present, was probably smaller than today. Indeed, the paleotemperature data from ODP Site 847 suggest that the cold tongue expanded toward its present configuration in the interval from ~1.8 to ~1.2 Ma (*7*), during what would appear to be a time of relatively stable polar climate and glacial ice volume (*12*). If the development of the modern cold tongue was driven by thermocline shoaling, it should have been accompanied by an equatorward contraction of the thermocline's polar margins, which is a second expression of the volume of warm ocean water (*5*, *6*). However, the paleoceanographic

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test of this prediction has awaited the development of continuous high-latitude SST reconstructions, especially from the Southern Hemisphere, which is particularly important in the ventilation of the global thermocline. Here, we report two high-resolution Pliocene-Pleistocene paleotemperature records from the northern and southern subpolar regions, which provide strong evidence in favor of this contraction of the subtropical ocean. Such findings support the existence of a pervasive link between the cooling and equatorward expansion of subpolar and polar conditions and the emergence of the modern cold tongue in the equatorial Pacific at the beginning of the Pleistocene.

The two paleotemperature records presented in this study are based on the analysis of alkenone unsaturation indices (*13*, *14*) in sediments from ODP Sites 882 (sub-Arctic Pacific) and 1090 (sub-Antarctic Atlantic) (Fig. 1). The percentage of the $C_{37:4}$ alkenone relative to the total abundance of C_{37} alkenones (%$C_{37:4}$) in these records (Fig. 2, D and E) is an additional tracer that can be used to infer variations in the meridional extent of polar and subpolar conditions through time (*15*–*18*).

The long-term trend of the SST records reveals a major subpolar cooling from ~1.8 to ~1.2 Ma, with an average bipolar temperature drop of 4° to 5°C (Fig. 2, B and C). This coincides with an increase in the %$C_{37:4}$ alkenone in both sites, indicating a progressive expansion of the polar waters into the present-day sub-Arctic and sub-Antarctic regions (Fig. 2, D and E). These findings are in good agreement with the onset of a progressive increase in biogenic opal mass accumulation rates observed in the Southern Ocean around the Polar Front, the Polar Front Zone, and the Subtropical Front during this time interval (*19*). Micropaleontological data from the Southern Ocean indicate that a temperature drop of 5° to 6°C in the sub-Antarctic Atlantic during the Last Glacial Maximum (LGM) was associated with an expansion of winter sea ice in the Atlantic sector of the Southern Ocean from 55°S to ~47°S (*20*). If most of the Pliocene glacial SSTs were 4° to 5°C warmer than LGM temperatures, then Antarctic sea ice cover during Pliocene glacial stages may have been more similar to the present-day distribution than to the LGM distribution. In this sense, the end of the subsequent cooling transition around 1.2 Ma can be considered to mark the establishment of an Antarctic sea ice field comparable to that during the LGM.

The pronounced subpolar cooling and the associated sea ice expansion resulted in an increase in the meridional temperature gradient between the subpolar regions and the equatorial Pacific, changing from around 14° to 15°C in the Pliocene to the 19° to 20°C characteristic of the present-day ocean in the case of the western Pacific, and from 11° to 12°C in the Pliocene to the present gradient of 13° to 14°C in the eastern Pacific (Fig. 2F). A weaker meridional temperature gradient in the early Pliocene implies an expanded tropical warm pool and consequently a weakening and poleward expansion of the Hadley atmospheric convective cells (*6*). Our data suggest that this vast tropical warm pool persisted until the end of the Pliocene at 1.8 Ma.

Remarkably, our data show that the temporal evolution of the meridional temperature gradients between the subpolar regions and the equatorial Pacific mirrors the strengthening of the zonal (east-west) equatorial Pacific temperature gradient (from ~1.8 to ~1.2 Ma) that led to the expansion of the equatorial Pacific cold tongue toward its present-day configuration, and to the development of the modern mode of the Walker circulation system (*7*, *8*) (Fig. 2F). As recently shown by Brierley *et al.* (*6*), the meridional expansion of the warm pool provides a crucial mechanism to sustain a deeper thermocline in the equatorial Pacific during the Pliocene through its effect on the temperature of the thermocline waters in the subtropical subduction zones. Our findings indicate that, in fact, the subsequent expansion of the polar oceans and the associated contraction of the warm pool was closely coupled to the development of the modern cold tongue in the equatorial Pacific, providing strong empirical support for the existence of a direct link between the strengthening of the meridional temperature gradients and the shoaling of the thermocline in the eastern equatorial Pacific.

In addition, our data from ODP Site 1090 indicate that the subpolar cooling transition was linked to a major shift in the response of sub-Antarctic climate to Earth's orbital variations from a subtropical to a subpolar pattern, consistent with an equatorward expansion of the polar and subpolar frontal systems and an associated contraction of the subtropical gyres at the beginning of the Pleistocene. The record of glacial/interglacial sub-Antarctic Atlantic temperature variability during the past 800,000 years is in good agreement with the paleoclimatic reconstructions of the Antarctic ice core records (*21*–*23*), showing a dominant obliquity (41,000-year) cycle during the mid-Pleistocene, a progressive increase in the power of the 100,000-

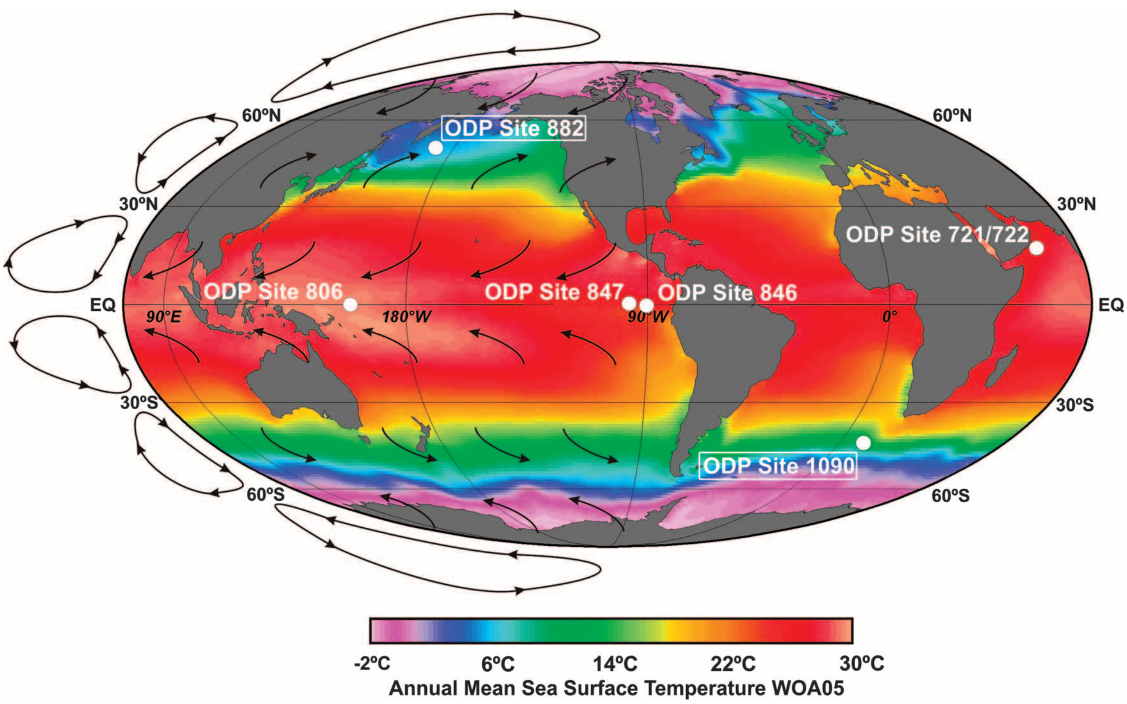

Fig. 1. Location of ODP Site 1090 (42°54.5′S, 8°54.0′E; water depth 3702 m), ODP Site 882 (50°21′N, 167°35′E, water depth 3244 m), and other records discussed in the text. Black arrows are schematic representations of the atmospheric convective cells and wind direction. Modern annual mean SST values are from the World Ocean Atlas 2005 (WOA05). [Map generated with Ocean Data View software, http://odv.awi.de]

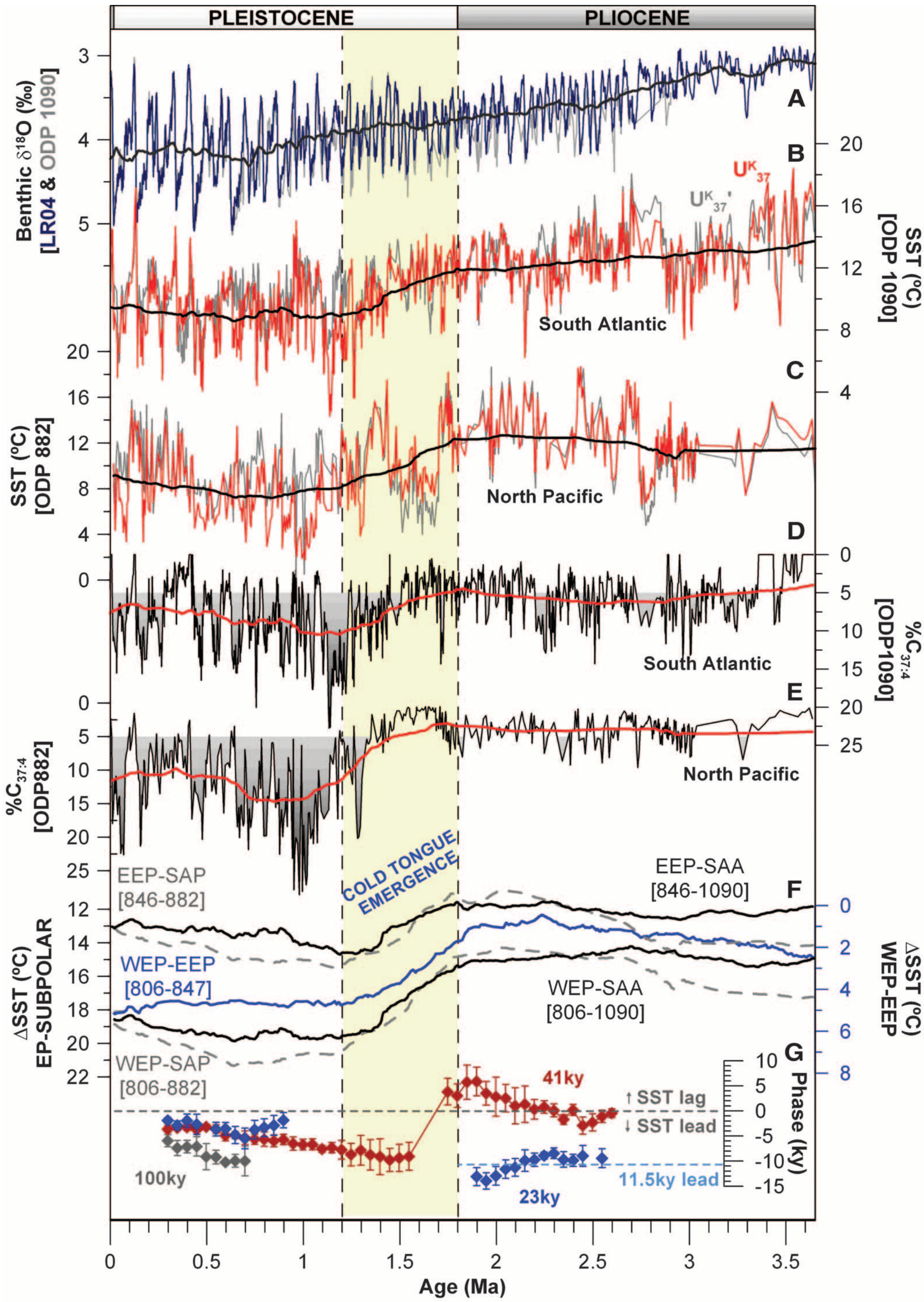

Fig. 2. Pliocene-Pleistocene evolution of the subpolar oceans, global ice volume, and meridional temperature gradients. (**A**) Lisiecki and Raymo (LR04) benthic $\delta^{18}O$ stack (*12*) (blue) and ODP Site 1090 benthic $\delta^{18}O$ reconstruction (*30*) (gray). (**B** and **C**) SST reconstructions using alkenone unsaturation indices, U^{K}_{37} (red line) and $U^{K'}_{37}$ (gray line), from ODP Site 1090 in the sub-Antarctic Atlantic (SAA) (B) and ODP Site 882 in the sub-Arctic Pacific (SAP) (C). (**D** and **E**) Latitudinal extension of the polar waters into the SAA (D) and the SAP (E), inferred from the percentage of tetra-unsaturated alkenone relative to the total abundance of unsaturated C37 alkenones (%$C_{37:4}$). (**F**) Evolution of the longitudinal and latitudinal SST gradients estimated by subtracting 400,000-year smoothed curves of ODP Site 806 for the western equatorial Pacific (WEP) (*7*), ODP Sites 846 (*10*) and 847 (*7*) for the eastern equatorial Pacific (EEP), ODP Site 882 for the SAP, and ODP Site 1090 for the SAA. (**G**) Phase relationships between ODP Site 1090 benthic $\delta^{18}O$ and alkenone SST for the intervals where the two series are coherent above the 80% confidence level. Phase, coherency estimates, and errors (± SD) were calculated using the iterative spectral feature of the Arand software package with a 600,000-year window and 300 lags. ky, thousands of years.

year cycle toward the present, and secondary precession (23,000- and 19,000-year) cycles (Fig. 3C). Moreover, variations in sub-Antarctic Atlantic temperatures lead changes in continental ice volume (inferred from $\delta^{18}O$) by around 3200 years at the precession frequency band. This likely corresponds to a phase lag of around 1600 years with respect to Northern Hemisphere insolation (*12*), in good agreement with the estimates obtained from the independently dated Antarctic ice cores [i.e., ~1800 years (*22*)]. However, before 1.6 Ma, the temperature variability of the sub-Antarctic Atlantic was distinctly different, with an increased power of precession with respect to obliquity (Fig. 3, B and C), a clear Southern Hemisphere insolation forcing of sub-Antarctic Atlantic temperature at the precession frequency band (*24*), and an in-phase behavior with respect to $\delta^{18}O$ at the obliquity band (Fig. 2G), which is indicative of a shift toward low-latitude insolation forcing of sub-Antarctic Atlantic climate during this period. These findings suggest that the equatorward contraction of the subtropical gyres at the beginning of the Pleistocene caused the sub-Antarctic Atlantic climate to become less sensitive to (precession-driven) variations in Southern Hemisphere low-latitude insolation forcing and more sensitive to (obliquity-driven) variations in Antarctic climate around 1.6 Ma (*25*). This interpretation is supported by a decrease in precession signal observed in African continental climate records subsequent

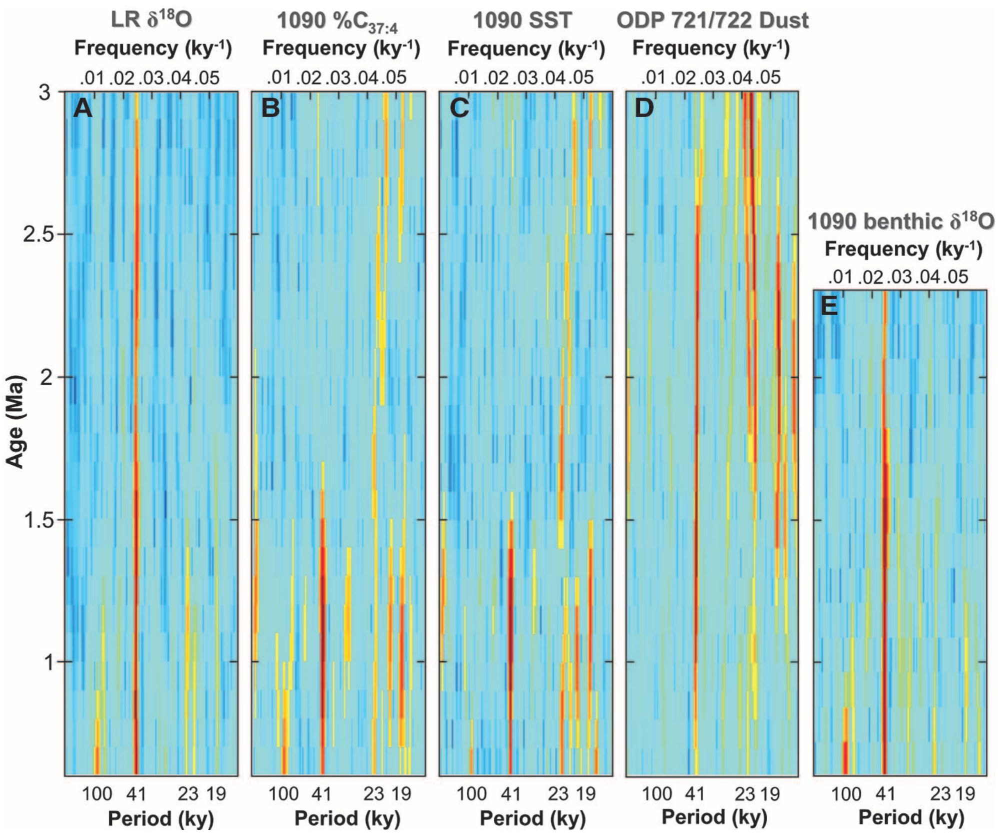

Fig. 3. Evolutionary Blackman-Tukey power spectra of (**A**) LR04 global benthic $\delta^{18}O$ stack (*12*), (**B**) ODP Site 1090 $\%C_{37:4}$, (**C**) ODP Site 1090 SST, (**D**) ODP Site 721/722 dust flux reconstruction (*28*), and (**E**) ODP Site 1090 benthic $\delta^{18}O$ record (*30*). The evolutionary power spectra of all the records was computed using the short-time Fourier transform of overlapping segments with a 600,000-year Hamming window and 90% overlap. Before spectral analysis, all series were detrended, interpolated to 2000-year intervals (ky, thousands of years), and prewhitened to minimize the interference of low-frequency variability.

to 1.8 to 1.6 Ma (Fig. 3D) (*26*–*28*). A shift in Southern Ocean biology is also recorded around 1.6 Ma, marked by the onset of massive *Fragilariopsis kerguelensis* (diatom) deposition (*29*) and the development of extensive diatom mats between 47° and 50°S (*29*).

Why the cold tongue expanded toward its present-day configuration around 1.8 to 1.2 Ma, during what would appear to be a time of relatively stable polar climate and glacial ice volume, has been a long-standing question. Our data show that the tropics were not alone in changing at this time, with a bipolar cooling and equatorward expansion of the subpolar water masses also occurring. Thus, our data appear to confirm the hypothesis that the expansion of the subpolar oceans shoaled the thermocline and thus led to the emergence of the modern cold tongue. The converse causation, with the equatorial Pacific driving subpolar changes, lacks the same grounding in dynamical expectations (*4*).

Under anthropogenic forcing of climate, the high latitudes appear to be responding faster than elsewhere—a dynamic that fits with expectations. Given the close link demonstrated here between subpolar ocean climate and the equatorial Pacific, the cold tongue may also respond to the ongoing warming. Indeed, it seems plausible that a warming-driven deepening of the thermocline could result in a reduction or even loss of the cold tongue, initiating a warm state in the Pacific tropical ocean that is reminiscent of the Pliocene.

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