

## CLIMATE CHANGE

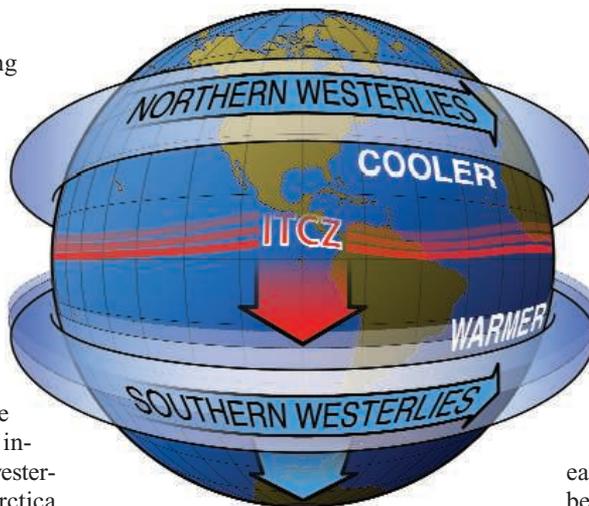
## Shifting Westerlies

J. R. Toggweiler

The westerlies are the prevailing winds in the middle latitudes of Earth's atmosphere, blowing from west to east between the high-pressure areas of the subtropics and the low-pressure areas over the poles. They have strengthened and shifted poleward over the past 50 years, possibly in response to warming from rising concentrations of atmospheric carbon dioxide (CO<sub>2</sub>) (1–4). Something similar appears to have happened 17,000 years ago at the end of the last ice age: Earth warmed, atmospheric CO<sub>2</sub> increased, and the Southern Hemisphere westerlies seem to have shifted toward Antarctica (5, 6). Data reported by Anderson *et al.* on page 1443 of this issue (7) suggest that the shift 17,000 years ago occurred before the warming and that it caused the CO<sub>2</sub> increase.

The CO<sub>2</sub> that appeared in the atmosphere 17,000 years ago came from the oceans rather than from anthropogenic emissions. It was vented from the deep ocean up to the atmosphere in the vicinity of Antarctica. The southern westerlies are important in this context because they can alter the oceanic circulation in a way that vents CO<sub>2</sub> from the ocean interior up to the atmosphere. The prevailing view has been that the westerlies shifted 17,000 years ago as part of a feedback: A small CO<sub>2</sub> increase or small warming initiated a shift of the westerlies toward Antarctica; the shifted westerlies then caused more CO<sub>2</sub> to be vented up to the atmosphere, which led to more warming, a greater poleward shift of the westerlies, more CO<sub>2</sub>, and still more warming (5). But Anderson *et al.* show that the westerlies did not shift in response to an initial CO<sub>2</sub> increase; rather, they shifted early in the climate transition and were probably the main cause of the initial CO<sub>2</sub> increase.

The strongest southern westerlies are found several hundred kilometers to the north of a broad oceanic channel that circles the globe around Antarctica. The stress from the westerlies on the ocean drives the Antarctic Circumpolar Current (ACC) through the channel. This stress also draws mid-depth water from north of



**Southward movement.** At the end of the last ice age, the ITCZ and the Southern Hemisphere westerlies winds moved southward in response to a flatter temperature contrast between the hemispheres (5, 6, 11). According to Anderson *et al.*, the northern westerlies may have also shifted to the south; this shift is not depicted in the figure.

the ACC to the surface around Antarctica. Over the past 50 years, the westerlies have shifted southward so that they are better aligned with the ACC and draw more mid-depth water to the surface than they did before (8, 9). At the peak of the last ice age, the opposite situation prevailed: The westerlies were so far north of today's position that they were no longer aligned with the ACC and could not draw much mid-depth water to the surface.

The mid-depth water upwelled by the westerlies is rich in CO<sub>2</sub> and in silica, a nutrient that fuels biological production in the surface waters around Antarctica. Siliceous remains of the organisms settle to the sea floor and accumulate in the sediments. Anderson *et al.* show that the accumulation of siliceous sediment increased dramatically during the transition out of the last ice age. They attribute this increase to a poleward shift of the westerlies that drew more CO<sub>2</sub>- and silica-rich water up to the surface.

A detailed analysis of the ice-core records from Antarctica shows that atmospheric CO<sub>2</sub> concentrations rose in two steps along with the air temperatures over Antarctica (10). The silica accumulation in Anderson *et al.*'s best resolved record also shows two pulses that correspond in time to the two steps (7). To create such a pulse in silica accumulation, larger quantities of sil-

ica-rich deep water must be drawn to the surface. As mentioned above, silica-rich deep water tends to be high in CO<sub>2</sub>. It is also warmer than the near-freezing surface waters around Antarctica.

A shift of the westerlies that draws more warm, silica-rich deep water to the surface is thus a simple way to explain the CO<sub>2</sub> steps, the silica pulses, and the fact that Antarctica warmed along with higher CO<sub>2</sub> during the two steps. Anderson *et al.*'s two silica pulses occur right along with the two CO<sub>2</sub> steps, which implies that the westerlies shifted early as the level of CO<sub>2</sub> in the atmosphere began to rise. Had the westerlies shifted in response to higher CO<sub>2</sub>, one would expect to see more upwelling and more silica accumulation after the second CO<sub>2</sub> step when the level of CO<sub>2</sub> is highest, but instead the silica accumulation drops back down.

What made the westerlies shift when they did? The answer seems obvious empirically but may be difficult to understand theoretically. The Northern Hemisphere is systematically warmer than the Southern Hemisphere, especially near the Atlantic Ocean, where the overturning circulation transports heat across the equator from south to north. As a result, Earth's thermal equator—the Intertropical Convergence Zone (ITCZ)—is north of the equator. The easterly trade winds that flank the ITCZ to the north and south are also skewed toward the Northern Hemisphere.

Anderson *et al.*'s two pulses of sediment accumulation took place along with Heinrich Event 1 and the Younger Dryas—events in which icebergs and melting glaciers flooded the North Atlantic with fresh water, thereby weakening the overturning. The weakened overturning cooled the Northern Hemisphere and warmed the Southern Hemisphere, thus reducing the temperature asymmetry. Sediment records from the southern Caribbean Sea show that the trade winds shifted to the south during the two pulses (11, 12). Thus, the ITCZ shifted closer to the equator and the southern westerlies apparently shifted toward Antarctica along with the southward movement of the trade winds (see the figure).

The sediment accumulation rate during Anderson *et al.*'s two pulses was five times as high as it was at the Last Glacial Maximum (just before the two pulses), and twice as high

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as it is today. This points to massive changes in the wind-driven upwelling around Antarctica during the transition out of the last ice age and suggests that the westerlies were closer to (or stronger next to) Antarctica during the transition than they are now.

Climate scientists have attributed changes in the westerlies over the past 50 years to the warming from higher CO<sub>2</sub>. The changes predicted by climate models in response to higher CO<sub>2</sub> are fairly small, however, and tend to be symmetric with respect to the equator. The observed changes have been quite asymmetric, with much larger changes

in the Southern Hemisphere than in the north (3). The results of Anderson *et al.* (7) suggest that in the past, the westerlies shifted asymmetrically toward the south in response to a flatter temperature contrast between the hemispheres. The magnitude of the shift seems to have been very large. If there was a response to higher CO<sub>2</sub> back then, it paled in comparison. Changes in the north-south temperature contrast today are not going to be as large as they were at the end of the last ice age, but even small changes could be an additional source of modern climate variability.

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## CHEMISTRY

# Inducing Chirality with Circularly Polarized Light

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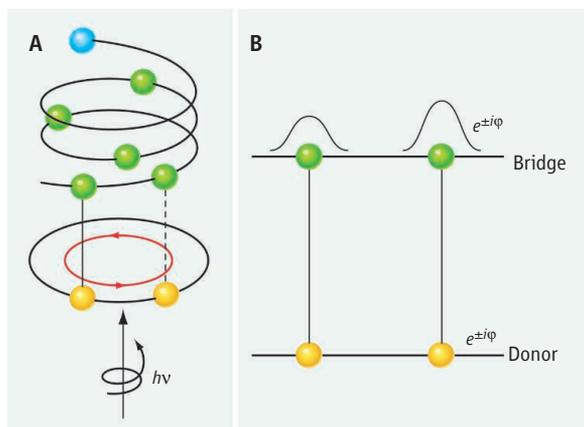
We have an intuitive understanding of how the shape and symmetry of objects affects their use from our hands. Each hand is chiral: Its mirror image (the right versus the left hand) is different from it. When we extend right hands, they can clasp because the thumbs point in opposite directions. A baseball bat fits equally well into either hand and does not work better for a right-handed hitter than a lefty. Similarly, we do not expect to see processes in molecules to be faster in the right-handed or left-handed versions, but a recent study of electron transfer induced by circularly polarized light rotating in a fixed direction reported unexpected differences in yields—on the order of several tenths of a percent—for molecules that differ only in their handedness (1). In a recent paper, Skourtis *et al.* (2) explain how these differences may arise through quantum interference when there are inequivalent pathways for electron transfer.

Electron transfer can occur within a molecule when light excites an electron at a donor site that then tunnels through the barrier set up by the bonds in the molecule to an acceptor site. The yield of electron transfer will depend on the width and height of the barrier, which is determined by the distance between the sites and the type of bonds in the intervening medium, called the bridge (3). A simple “tight-binding” model captures this distance dependence (4), and to a first approximation,

the rate will be faster the more the donor and acceptor states delocalize onto the bridge lowering the effective mass of the electron and leading to more efficient tunneling.

This delocalization is enhanced when bonding is strong between the donor, acceptor, and bridge, and the energies of the three sets of sites are close to one another. A model of a donor-bridge-acceptor system is shown in the figure, panel A, in which initially there is only a single bond between the donor and the

An unexpected difference in electron transfer rates for right- and left-handed versions of a molecule is caused by quantum interference.



**Inequivalent paths.** (A) A simple model for electron transfer mediated by a chiral structure, with a cyclic donor (atomic sites shown in yellow) attached via a single bond (solid line) or two bonds (solid and dashed lines) to a helical bridge (shown in green) terminated at its opposite end by an electron acceptor (shown in blue). Circularly polarized light (bottom, energy  $h\nu$ ) excites a ring current in a particular direction. (B) The circularly polarized light imparts a relative complex phase to the delocalization originating from the two ring sites. Different acceptor amplitudes (and thus different rates) arise from the two relative phases.

bridge (the solid line). In this tight-binding model, reversing the helicity of the bridge while preserving the bonding strength and relative energetics would yield equivalent electron transfer rates through the two possible bridge helicities.

How then can a preference for one bridge configuration be induced? In the Skourtis *et al.* model, circularly polarized light, which carries angular momentum, can excite ring currents that circulate in a particular direction in donors possessing degenerate electronic states—states of the same energy and similar shapes (5). For the simple model of atoms on a ring, excitation with circularly polarized light yields equal electron density at each ring site, but the amplitudes at the various sites differ in their complex phase (6).

Reversing the polarization of the light reverses the direction of the ring current. The electron density remains unchanged, but the opposite handedness of the light produces different relative phases between sites. However, excitation of either current direction would still yield no preference for transfer through the helical bridge because the electron density at the site connecting the donor to the bridge is unchanged.

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