However, the partitioning of the waveforms in our data set increases the variance of the observations, currently limiting the ability of this approach to resolve lateral variations in scattering strength.

REFERENCES AND NOTES

10. Our data, spanning 1988 through 1995, were obtained by means of the IRIS Fast Archive and Recovery Method (FARM). The FARM database contains shallow events (<100 km) with moment magnitude (Mw) ≥5.8 and deep events (>100 km) with Mw ≥5.5.
12. Including seismograms with impulsive noise bursts resulting from unrelated earthquakes or instrument error would contaminate the stacked image. Seismograms containing such artifacts were removed by visual inspection. In addition, possible contamination from double events was further avoided by removing traces with impulsive energy arriving before the theoretical arrival. Other seismic phases, including SS, SP, and SPP, overlap a portion of the time-distance window in which the precursors were imaged. However, these phases have a different move-out and are not concentrated in the high frequencies (7) because of the high attenuation of the S phase.
13. Eighty-nine percent of the CMB is within 10° of a velocity layer (# Mantle, taking the form of an ultra–low-velocity layer at the base of the mantle. J. Revenaugh* and R. Meyer

Seismic Evidence of Partial Melt Within a Possibly Ubiquitous Low-Velocity Layer at the Base of the Mantle

Three source regions show evidence of a low-velocity layer that is less than 15 kilometers thick on top of the core-mantle boundary and require about a 3:1 ratio of shear-to-compressional velocity reduction, which is consistent with partial melt. Layer thickness is correlated with travel time residuals of the seismic phases that are most sensitive to the lowest mantle velocity. These observations suggest that the layer is thinned beneath downwellings but is present everywhere along the core-mantle boundary. Low viscosity accompanying partial melt can localize the upwelling of warmed mantle, making the low-velocity layer a plausible source of mantle plumes.

Recent seismic work has mapped several anomalously slow regions of the lowest mantle, taking the form of an ultra–low-velocity layer ≤40 km thick on top of the core-mantle boundary (CMB) (1, 2). P wave velocity (vP) within the layer is as much as 10% lower than that of the overlying mantle. Partial melt offers an explanation of the layer (3) and predicts a 30% shear wave velocity (vS) drop within the layer (3, 4). Because the CMB approximates an isotherm, this hypothesis also predicts layer ubiquity in the absence of substantial compositional heterogeneity. We tested these predictions by searching for reflections from the layer in seismograms recorded by California regional arrays. PnP, the high-frequency compressional-wave reflection from the CMB, is often used to study the detailed structure of the boundary (5). Its typically low signal-to-noise ratio necessitates the use of array data to avoid misinterpretation of noise as an anomalous structure. Precursors to PnP due to reflection or scattering from lowermost mantle structures are further buried in noise (2, 6). To detect them and measure their amplitude at 5 AUGUST 1997
Means, standard deviations, and ranges of the adjustable parameters for the acceptable model subset.

**Table 1.**

<table>
<thead>
<tr>
<th>Source region</th>
<th>Events (n)</th>
<th>Records (n)</th>
<th>PcP</th>
<th></th>
<th>PdP</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>d (km)</td>
<td>R (s)</td>
<td>σ (s)</td>
<td>d (km)</td>
</tr>
<tr>
<td>TF</td>
<td>111</td>
<td>4217</td>
<td>2895 ± 7</td>
<td>0.01 to 0.13</td>
<td>0.05 ± 0.03</td>
<td>0.00 to 0.13</td>
</tr>
<tr>
<td>UK</td>
<td>83</td>
<td>2892</td>
<td>2893 ± 9</td>
<td>0.00 to 0.13</td>
<td>0.02 ± 0.02</td>
<td>0.00 to 0.13</td>
</tr>
<tr>
<td>SA</td>
<td>52</td>
<td>1607</td>
<td>2887 ± 6</td>
<td>0.00 to 0.11</td>
<td>0.02 ± 0.02</td>
<td>0.00 to 0.12</td>
</tr>
</tbody>
</table>

Fig. 1. Mercator projection showing the earthquakes (triangles), stations of the California regional seismic networks (inset; dots), and outlines of the CMB bouncing PcP phases, each containing an average of 512 bounce points.

Fig. 2. (A) Stack of 5509 seismograms for events in the TF subduction complex for target reflectors in the lowermost mantle (solid line). Only a single midpoint bin was used, which ignored structural variation near the bounce points of PdP. Gray shading denotes 95% confidence intervals of the data stack as determined by the bootstrap method. Synthetic stack (dashed line) contains only PcP arrivals. (B) As in [A], except that data were separately stacked in five 3° by 3° bounce point bins and aligned before final stacking. (C) Binned stack of 2892 seismograms of events in the TF subduction complex. (D) Binned stack of 1607 seismograms of events in SA. Note the normal-polarity, closely spaced precursor to PcP (arrow).

and phase, we used a stacking algorithm that, unlike traditional and double-beam forming (7), presupposes a target phase. Here that phase is PdP, a PcP-like reflection from a lower mantle discontinuity.

Defining τ_{ij}^P as the travel time of P for the ith event recorded by the jth station and τ_{ij}^{PdP} (d) as the arrival time of PdP reflected from a discontinuity at depth d (8), we obtained the stack from

\[ R(d) = \sum_i \sum_j S_i (t_i) \tau_{ij}^P + \tau_{ij}^{PdP} (d) - \tau_{ij}^P \]  

where the seismograms S_i (t) (where t is time) are aligned with P at time t_i and R is the mean reflector strength (9). When the source and receiver arrays are small and the paths of P and PdP are similar, the amount of stack degradation due to travel time heterogeneity is small. As used here, both arrays are large, and the paths of P and PdP diverge by as much as 1000 km. To reduce the effect of incoherence on the stack, we summed wave forms in small PdP bounce-point bins that measure 2° to 6° on a side (Fig. 1). Once obtained, these bin stacks were aligned on peak observed time and summed to produce a final composite stack. Alignment on peak amplitude is justified by the consistency of stack shape and the small dispersion of peak amplitude depths (<20 km, equivalent to travel time shifts of <1 s). Bins with fewer than 150 hits or poorly defined peaks were not summed. Modeling with randomly time-shifted synthetic data suggests no more than ±0.6 s of remaining travel time variability.

For the Tonga-Fiji (TF) subduction complex, a peak above the 95% confidence level in the lowermost mantle was identified as PcP, and a precursory shallow trough was identified as a reverse-polarity reflection (the sign opposite of P and PcP) from a discontinuity about 14 km above the CMB (Fig. 2A). A precursor is needed to explain the stack because, although the stacked synthetic PcP wave form is slightly asymmetric (10), the magnitude of the shallow trough is much less than observed and it is not possible for us to mimic the trough simply by summing variably delayed PcP phases. This is consistent with a previous study of this region that modeled wave forms for two nearly co-located events included in our data set (2). The primary difference between our results and those of (2) is in the peak stack amplitude, which is only 2.5% of P in this study. We take this as evidence of stack degradation due to travel time heterogeneity.

Peak PcP amplitude depths range from 27 to 11 km below the CMB in the five bin stacks for events in TF (Fig. 1), signifying a delayed PcP arrival and lower-than-average velocities in D*, the lowermost 200 to 300 km of the mantle (Fig. 2B). Peak aligned stack amplitude is increased over that of the nonbin stack, and there is noticeable compaction of the stack peaks, which indicates reduction in travel time variability due to binning.

To estimate the mean depth, reflection coefficient, and remaining travel-time variability of PcP and the precursory PdP phase, 20,000 Monte Carlo synthetic data sets were generated, stacked, and compared with the observed stack. For PcP and PdP, there exist trade-offs between R and the travel-time variability (σ) (11). There is also a trade-off between R and the thickness of the layer [the low-velocity layer (LVL)] separating the CMB from the PdP reflector (H_{LVL}) because PcP and PdP are separated in time by less than the dominant period (~1 s). Models were accepted if they accounted for greater than 80% of stack variance, a value chosen with reference to the
acceptable models is large, it also appears
good, or (3) a residual, no-net-velocity, slit of
and long-wavelength diffracted P velocity
It would appear that the stack for SA
IAV, and seismically very slow layer
S lower boundary of the LVL (18), a thick,
result between the D" velocity structure and

Fig. 3. (A) Dots indicate acceptable velocity varia-
tions across a first-order discontinuity that is

SA events (Fig. 2D) shows that the pre-
cursory phase is not reversed and arrives
close to PcP. These observations are borne
out by the Monte Carlo simulations, which
have a mean layer thickness of 8 ± 3 km and PdP
reflection coefficients ranging from −0.03 to 0.12
with a mean value of 0.02 (Table 1).

For the TF and IJK stacks (Fig. 2, B and C),
all acceptable models have reversed-polarity
PdP. The amplitude of PdP relative to P can
be used to estimate the velocity and density
contrasts of the reflector. A grid search was
conducted over $v_N$, $v_P$, and density
perturbations, in which a mean reflection
coefficient was computed for each per-
turbation triplet (12). Triplets predicting R
into a factor of 2 of the observed range
of PdP reflection strengths were accepted
(13). Both $v_N$ and $v_P$ must drop across
the layer to produce the observed reversed po-
larity reflections (Fig. 3, A and C). Further-
more, a nearly 3:1 ratio of $v_N$ to $v_P$ decrease
is needed. Density was allowed to vary be-
tween −3% and 10% and was found to have
little effect on the sign or magnitude of
computed reflection coefficients. We also
directed the effects of a 5-km-wide PdP
transition for the TF source region (14).
The effect of a broadened transition is to
increase the minimum acceptable velocity
perturbations and the range of acceptable $v_N$
to $v_P$ ratios (Fig. 3B).

Analysis of PcP precursor amplitudes
requires about a 3:1 ratio of $v_N$ to $v_P$
decrease in a thin layer on top of the CMB.
Our modeling approach does not constrain
the absolute drops, but work with core-diffract-
ed phases in other areas (1) requires as large
as 10% $v_P$ drops within the LVL. Extrapo-
lat ing those results to this study suggests $v_P$
drops of 30 to 50%. These numbers are
consistent with the presence of partial melt
(3, 4). Whether similar ratios can be
achieved solely by compositional variation,
such as iron enrichment in a basal mixing
layer (3, 16), is uncertain.

An inverse relation exists between $H_{LVL}$
and long-wavelength diffracted P velocity
($v_{P_{dP}}$) (17) in D" (Fig. 4A). The layer is
thicker in regions of low $v_{P_{dP}}$ consistent
with depressed $v_P$ within it. We observed
a similar correlation between $v_{P_{dP}}$ and PcP
time-travel delays ($\delta t_{P_{dP}}$) (Fig. 4B). The
magnitudes of the inferred $\delta t_{P_{dP}}$ are larger
by a factor of 2 than those that would be
produced by a thin ($\approx$15 km) layer with a
10% $v_P$ decrease, which implies a correla-
tion between the D" velocity structure and
the basal layer thickness in which the layer is
thickened under upwellings (TF) and
thinned under downwellings (SA) but is
potentially ubiquitous.

Although the large errors preclude any

sort of quantitative analysis, we note that
the estimates of range-adjusted mean PdP
reflection coefficients decrease as the layer
thins, implying diminished velocity drops
within the basal layer. If melt rains down
from the overlying mantle (18), a thick,
melt-rich, and seismically very slow layer
would accumulate beneath hot D" and
mantle upwelling, whereas a thin melt-poor
layer would accumulate beneath downwell-
ings. This does not, however, account for
the sharp upper boundary of the LVL (2).

An alternative is iron enrichment within
the LVL. Chemical reactions between silicate
liquids and iron readily occur (19). An
LVL partially isolated from general mantle
circulation by negatively buoyant melt and
low viscosity (20) could become iron-en-
riched, increasing density and further
decreasing seismic velocities (3). Lateral flow
within the LVL could collect iron-rich ma-
tle material beneath upwellings, relating
layer thickness to velocity drop.

Models of deep-mantle plume formation
emphasize the role of a thin low-viscosity
channel (21). With increasing thermal age,
the channel thickens, becomes dynamically
unstable, and eventually erupts hot materi-
Al. We suggest that the partially molten
LVL, with its attendant low viscosity, is this
channel and is thus a source of mantle
plumes.

REFERENCES AND NOTES
1. E. Gamero and D. V. Helmberger, Phys. Earth Plan-
et. Inter. 91, 161 (1995); Geophys. Res. Lett. 23, 977
(1996); E. Gamero, S. Grand, D. V. Helmberger, ibid.
2. J. Mori and D. V. Helmberger, J. Geophys. Res. 100,
3. Q. Williams and E. J. Gamero, Science 273, 1528
(1996).
The occurrence of long-range electron transfer (ET) in duplex DNA remains controversial (1). Does the π system of stacked base pairs in B-form DNA function as a molecular wire or as an insulator? Barton and co-workers (2–5) have reported several lines of evidence in support of efficient long-range ET involving an electronically excited intercalated metal complex and either a second intercalated metal complex or a “natural” electron donor such as guanine or thymine dimer. The observation of efficient fluorescence quenching in systems with randomly intercalated metal complexes (2) and a synthetic 15–base pair duplex in which a donor complex was tethered to the 5′ end of one oligomer and an acceptor complex was tethered to the 5′ end of its complement (3) was attributed to the occurrence of long-range ET. This interpretation has recently been questioned on both experimental (6–8) and theoretical (9) grounds. Current commentaries on this controversy have pointed out the need to determine systematically the dependence of the ET rate constant on the distance separating the donor and acceptor in a series of structurally well-defined supramolecular systems in which the ET process can be directly monitored (1).

We report here the results of our investigation of the distance dependence of the photoinduced ET in a family of synthetic DNA hairpins in which a stilbene dicarboxamide forms a bridge connecting two oligonucleotide arms. Investigation of the fluorescence and transient absorption spectra of these hairpins established that no photoinduced electron transfer occurs for a hairpin that has six deoxyadenosine-deoxythymidine base pairs. However, the introduction of a single deoxyguanosine-deoxyxytidine base pair resulted in distance-dependent fluorescence quenching and the formation of the stilbene anion radical. Kinetic analysis suggests that duplex DNA is somewhat more effective than proteins as a medium for electron transfer but that it does not function as a molecular wire.

Distance-Dependent Electron Transfer in DNA Hairpins

Frederick D. Lewis,* Taifeng Wu, Yifan Zhang, Robert L. Letsinger, Scott R. Greenfield, Michael R. Wasielewski

The distance dependence of photoinduced electron transfer in duplex DNA was determined for a family of synthetic DNA hairpins in which a stilbene dicarboxamide forms a bridge connecting two oligonucleotide arms. Investigation of the fluorescence and transient absorption spectra of these hairpins established that no photoinduced electron transfer occurs for a hairpin that has six deoxyadenosine-deoxythymidine base pairs. However, the introduction of a single deoxyguanosine-deoxyxytidine base pair resulted in distance-dependent fluorescence quenching and the formation of the stilbene anion radical. Kinetic analysis suggests that duplex DNA is somewhat more effective than proteins as a medium for electron transfer but that it does not function as a molecular wire.

The occurrence of long-range electron transfer (ET) in duplex DNA remains controversial (1). Does the π system of stacked base pairs in B-form DNA function as a molecular wire or as an insulator? Barton and co-workers (2–5) have reported several lines of evidence in support of efficient long-range ET involving an electronically excited intercalated metal complex and either a second intercalated metal complex or a “natural” electron donor such as guanine or thymine dimer. The observation of efficient fluorescence quenching in systems with randomly intercalated metal complexes (2) and a synthetic 15–base pair duplex in which a donor complex was tethered to the 5′ end of one oligomer and an acceptor complex was tethered to the 5′ end of its complement (3) was attributed to the occurrence of long-range ET. This interpretation has recently been questioned on both experimental (6–8) and theoretical (9) grounds. Current commentaries on this controversy have pointed out the need to determine systematically the dependence of the ET rate constant on the distance separating the donor and acceptor in a series of structurally well-defined supramolecular systems in which the ET process can be directly monitored (1).

We report here the results of our investigation of the distance dependence of the photoinduced ET in a family of synthetic DNA hairpins in which a stilbene dicarboxamide forms a bridge connecting two oligonucleotide arms. One of our laboratories previously described the synthesis of thermodynamically stable stilbene-containing hairpins with stems consisting of three or more dA-dT or dG-dC base pairs (10). Hairpins with dA-dT stems are fluorescent, whereas hairpins with dG-dC stems are nonfluorescent. Photoinduced ET from guanine to the stilbene singlet state provides a plausible but untested mechanism for fluorescence quenching. Because the transient absorption spectra of both the stilbene singlet state (11) and its anion radical