

ture containing 0.3 percent water at 100°C led to deceleration and cessation of the enzymatic transesterification [because of the water-induced destabilization of the biocatalyst (Fig. 2B)].

On the basis of these data, the structure of the dry lipase, although similar to that of its wet counterpart (12), appears to be more rigid. If so, then even though the wet porcine pancreatic lipase [an enzyme known for its wide substrate specificity (5)] will accept nearly any alcohol as a nucleophile in the transesterification reaction, the dry lipase will perhaps be unreactive toward bulky alcohols because it lacks the conformational mobility needed to accommodate them in the active center. To test this prediction, we examined the reaction of tributyrin with various alcohols (Table 1) catalyzed by dry and wet lipase. Upon increase in size or transition from primary to secondary alcohol, the reactivities of the wet and dry enzyme remained comparable. However, with tertiary alcohols the dry lipase, in contrast to the wet, was completely inactive (Table 1). Thus, dehydration of the enzyme not only enhances its thermal stability but also changes its substrate specificity (13). This phenomenon, should it prove to be a general one, may form a basis for a new approach to the improvement of catalytic properties of enzymes (14).

ALEKSEY ZAKS

ALEXANDER M. KLIBANOV*

Laboratory of Applied Biochemistry,
Department of Nutrition and Food
Science, Massachusetts Institute of
Technology, Cambridge 02139

References and Notes

1. W. Kauzmann, *Adv. Protein Chem.* **14**, 1 (1959); C. Tanford, *Physical Chemistry of Macromolecules* (Wiley, New York, 1961); G. E. Schulz and R. H. Schirmer, *Principles of Protein Structure* (Springer-Verlag, New York, 1979); C. R. Cantor and P. R. Schimmel, *Biophysical Chemistry* (Freeman, San Francisco, 1980), part 1.
2. R. E. Feeney, in *Chemical Deterioration of Proteins*, J. R. Whitaker and M. Fujimaki, Eds. (American Chemical Society, Washington, D.C., 1980), p. 1; A. M. Klibanov, *Adv. Appl. Microbiol.* **29**, 1 (1983).
3. E. Antonini, G. Carrea, P. Cremonesi, *Enzyme Microb. Technol.* **3**, 291 (1981); M. D. Lilly, *J. Chem. Tech. Biotech.* **32**, 162 (1982); K. Martinek, A. V. Levashov, Yu. L. Khmel'nitsky, N. L. Klyachko, I. V. Berezin, *Science* **218**, 889 (1982); A. R. Macrae, *J. Am. Oil Chem. Soc.* **60**, 291 (1983); B. Cambou and A. M. Klibanov, *J. Am. Chem. Soc.* **106** (1984).
4. The porcine pancreatic lipase (E.C. 3.1.1.3) was obtained as a powder with a specific activity of 54 olive oil units per milligram of solid (Sigma). The water content in the commercial sample was determined (7) to be 3.6 percent.
5. P. Desnuelle, in *The Enzymes*, P. D. Boyer, Ed. (Academic Press, New York, ed. 3, 1972), vol. 7, p. 575; H. Bockerhoff and R. G. Jensen, *Lipolytic Enzymes* (Academic Press, New York, 1974).
6. The time course of the enzymatic transesterification was analysed by gas chromatography (measuring both disappearance of the alcohol and accumulation of the monoester) with the use of a 180-cm glass column packed with Super Pak 20M (Analabs).
7. H. A. Laitinen and W. E. Harris, *Chemical*

Analysis (McGraw-Hill, New York, ed. 2, 1975), p. 361.

8. Above 1.1 percent, the concentration of water begins to approach solubility in the tributyrin-heptanol mixture. Apparently as a result of some interfacial phenomena, the enzyme powder at the water content above 1.1 percent becomes a glue-like mass devoid of lipase activity.
9. P. L. Poole and J. L. Finney, *Int. J. Biol. Macromol.* **5**, 308 (1983).
10. C. Tanford, *Adv. Protein Chem.* **23**, 121 (1968); S. Lapanje, *Physico-chemical Aspects of Protein Denaturation* (Wiley, New York, 1978).
11. J. A. Rupley, E. Gratton, G. Careri, *Trends Biochem. Sci.* **8**, 18 (1983).

12. G. Careri, E. Gratton, P.-H. Yang, J. A. Rupley, *Nature (London)* **284**, 572 (1980).

13. The dry lipase remains inactive toward tertiary alcohols even when the temperature of the reaction mixture of tributyrin and a tertiary alcohol is raised from 20°C to 100°C. Thus a small amount of water acting as a "lubricant" seems to enhance the conformational mobility of the lipase molecule (presumably its active center area) to a greater extent than an 80° temperature increase from the ambient.
14. K. M. Ulmer, *Science* **219**, 666 (1983); T. H. Maugh II, *ibid.* **223**, 154 and 269 (1984).

* To whom correspondence should be addressed.

2 March 1984; accepted 23 March 1984

Satellite Observations of the 1982–1983 El Niño Along the U.S. Pacific Coast

Abstract. *Satellite infrared temperature images illustrate several effects of the 1982–1983 El Niño: warm sea-surface temperatures with the greatest anomalies near the coast, weakened coastal upwelling, and changes in surface circulation patterns. Phytoplankton pigment images from the Coastal Zone Color Scanner indicate reduced productivity during El Niño, apparently related to the weakened coastal upwelling. The satellite images provide direct evidence of mesoscale changes associated with the oceanwide El Niño event.*

The El Niño event that has caused major physical and biological changes in the equatorial Pacific since early 1982 began to affect the waters off California by December. Changes in surface and subsurface temperature, sea level, surface currents, and plankton have been noted (1, 2). Oceanographic data obtained fortuitously on previously scheduled cruises, at shore stations, or from sampling programs initiated in haste after the event had been recognized are

limited in spatial and temporal coverage. Global sea-surface temperature (SST) data analyzed routinely by the National Oceanic and Atmospheric Administration (NOAA) (3) provide good coverage, but only after averaging over large areas has removed energetic mesoscale features.

Fortunately, systematic sampling of the ocean surface has been carried out with a variety of sensors aboard orbiting satellites during the entire course of the

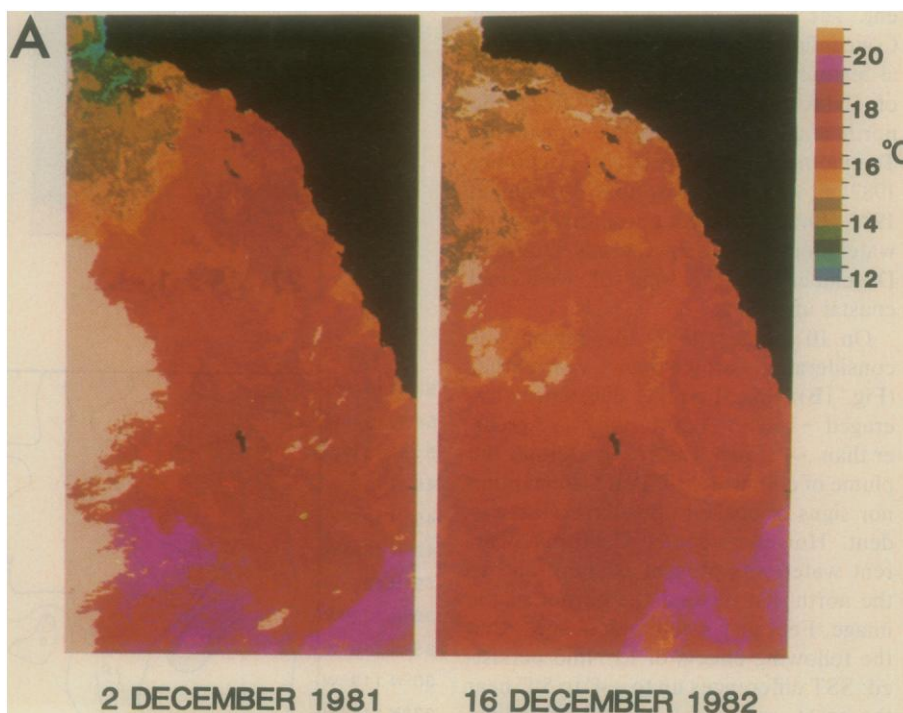


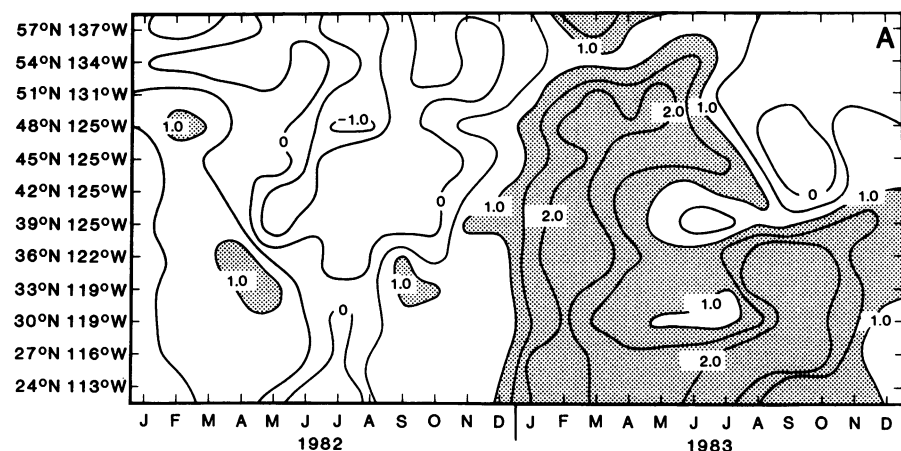
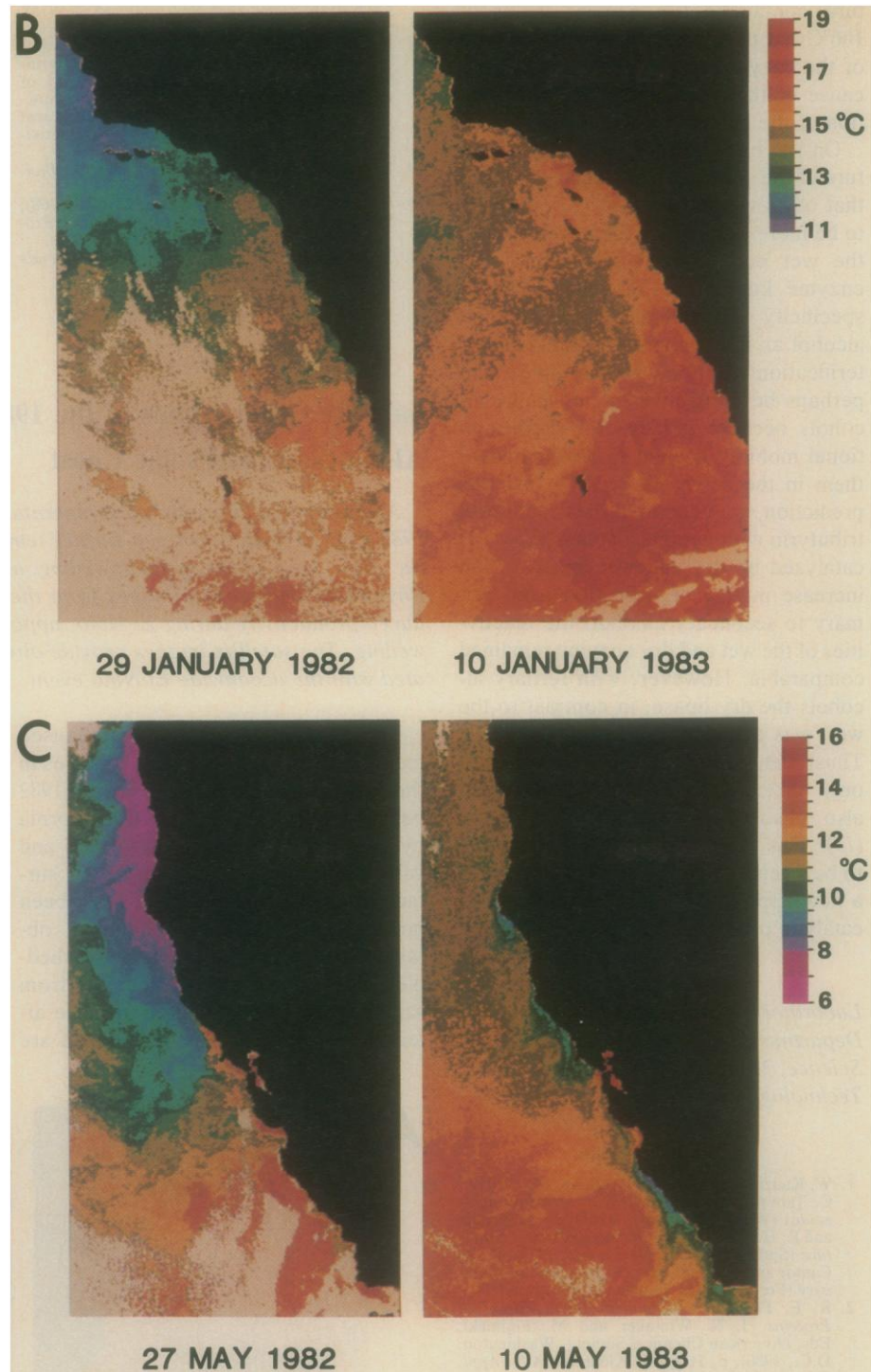
Fig. 1A. Advanced Very High Resolution Radiometer sea-surface temperature image off southern California.

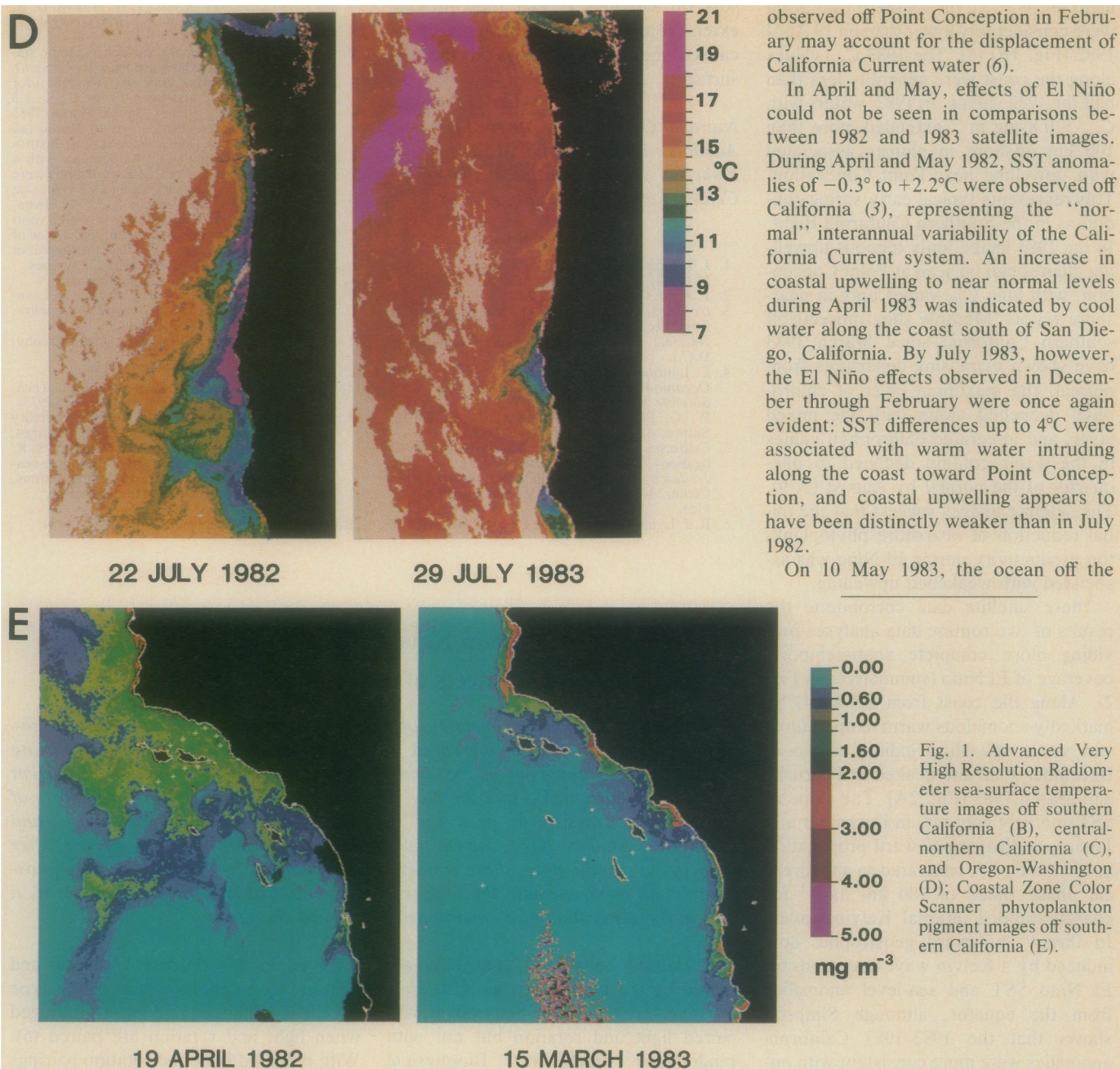
1982–1983 El Niño. These sensors provide extensive and synoptic coverage with resolution to 1 km^2 . Accurate estimates of SST can be retrieved from Advanced Very High Resolution Radiometer (AVHRR) infrared radiance data with sufficient precision to permit the detection of interannual changes. Satellite imagery of the SST field reveals changes in coastal upwelling intensity and circulation patterns, as well as gross SST anomalies.

The AVHRR data from daytime NOAA-7 passes (~ 1430 local time) were received and processed at Scripps Institution of Oceanography's Satellite Oceanography Facility. Calibration and multichannel SST retrieval were based on established and verified algorithms (4). The differential effect of water vapor in thermal-infrared channels 4 and 5 allows correction of the negative error caused by atmospheric absorption and reemission of infrared radiation from the sea surface. The matching of satellite SST estimates from 18 February 1982 with ship SST measurements from 35 stations off southern California occupied on the same day (5) yielded a root-mean-square deviation of $\pm 0.35^\circ\text{C}$ with a negligible bias of $+0.07^\circ\text{C}$.

On 16 December 1982, the ocean off the coast of southern California and northern Baja California was not consistently warmer than 1 year earlier (Fig. 1A): the mean and standard deviation of pixel-by-pixel SST differences were $-0.44^\circ \pm 0.89^\circ\text{C}$. However, striking differences in mesoscale features are apparent. The plume of cold water off Point Conception (top left corner) is a perennial feature formed by offshore advection of California Current water from the north augmented by coastal upwelling. The plume was still present in December 1982 but was warmer by up to 3°C than in 1981. Small patches of relatively cool water along the coast were less intense in December 1982, a sign of weakened coastal upwelling.

On 10 January 1983, this region was considerably warmer than 1 year earlier (Fig. 1B). Pixel-by-pixel differences averaged $+1.72^\circ \pm 1.20^\circ\text{C}$ and were greater than $+4^\circ\text{C}$ near the coast. Neither the plume of cold water off Point Conception nor signs of coastal upwelling were evident. However, cooler California Current water was present offshore and to the north just beyond the corner of the image. February satellite data show that the following effects of El Niño persisted: SST differences up to $+4^\circ$ to 5°C near the coast, very weak coastal upwelling, and no sign of a cold-water plume off Point Conception. An anomalously strong seasonal poleward countercurrent





observed off Point Conception in February may account for the displacement of California Current water (6).

In April and May, effects of El Niño could not be seen in comparisons between 1982 and 1983 satellite images. During April and May 1982, SST anomalies of -0.3° to $+2.2^{\circ}\text{C}$ were observed off California (3), representing the "normal" interannual variability of the California Current system. An increase in coastal upwelling to near normal levels during April 1983 was indicated by cool water along the coast south of San Diego, California. By July 1983, however, the El Niño effects observed in December through February were once again evident: SST differences up to 4°C were associated with warm water intruding along the coast toward Point Conception, and coastal upwelling appears to have been distinctly weaker than in July 1982.

On 10 May 1983, the ocean off the

Fig. 1. Advanced Very High Resolution Radiometer sea-surface temperature images off southern California (B), central-northern California (C), and Oregon-Washington (D); Coastal Zone Color Scanner phytoplankton pigment images off southern California (E).

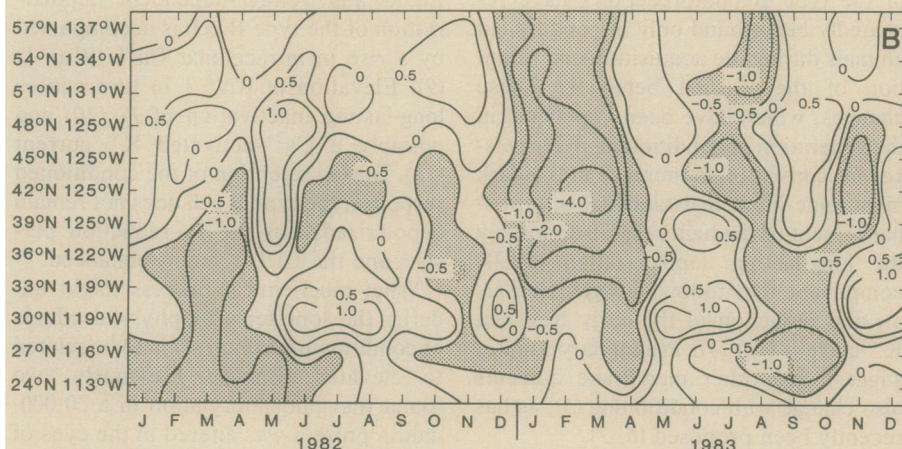


Fig. 2. Time series of 1982–1983 monthly anomalies along the Pacific coast. Monthly sea-surface temperature anomalies from 1942–1969 means (A) are from NOAA analyses of ship, buoy, and satellite data (3) averaged in 3° squares. Monthly upwelling index anomalies from 1946–1971 means (B) are normalized by the standard deviations of values published by Bakun (13). The upwelling index is equal to offshore Ekman transport, computed from surface wind stress vectors derived from synoptic analyses of the surface atmospheric pressure.

coast of central and northern California was not uniformly warmer than 1 year earlier (Fig. 1C). Pixel-by-pixel differences were $+1.58^{\circ} \pm 1.90^{\circ}\text{C}$ and up to $+5^{\circ}\text{C}$ north of San Francisco. However, coastal upwelling south of San Francisco appears to have been more intense in 1983, when SST was colder by up to 4.5°C than in 1982. On 29 July 1983, the ocean off the coast of Washington and Oregon was much warmer than 1 year earlier (Fig. 1D). Pixel-by-pixel differences were $+2.69^{\circ} \pm 1.99^{\circ}\text{C}$, with changes up to $+6.7^{\circ}\text{C}$ associated with weaker coastal upwelling.

The Coastal Zone Color Scanner (CZCS) on Nimbus-7 provides visible color data reflecting the biological effects of El Niño in terms of changes in phytoplankton biomass and productivity (7). On 15 March 1983, phytoplankton pig-

ment levels (C_{sat}) off southern California were considerably lower than on 19 April 1982 (Fig. 1E) (8). The 1983 C_{sat} values along the coast were generally less than half the 1982 values. In 1982, waters with $C_{\text{sat}} > 0.8 \text{ mg m}^{-3}$ extended more than 100 km offshore in plumes associated with upwelling near Point Conception. This represents typical early spring conditions in the Southern California Bight. In the 1983 image, only tenuous upwelling plumes can be seen at Point Conception, with high C_{sat} values only in near-shore waters. Monthly ship transects off southern California since March 1983 have shown increasing departures from normal: the maximum layer of chlorophyll deepened along with the mixed layer, and integrated chlorophyll values in the water column declined to one-quarter of the normal by August (2, 9). The satellite images suggest that the initial reduction of nearshore phytoplankton productivity during El Niño was associated with weakened upwelling.

These satellite data corroborate the results of two routine data analyses providing more complete spatiotemporal coverage of El Niño (summarized in Fig. 2). Along the coast from 27° to 49°N, markedly anomalous warm temperatures and weak upwelling indices began in December 1982 and peaked in February and March 1983 (Fig. 2A). The slope of SST anomaly contours in December and January indicates poleward propagation at 105 km day^{-1} , compared to a theoretical phase speed of 100 km day^{-1} for coastal trapped internal Kelvin waves. In theory, poleward geostrophic flow induced by a Kelvin wave may transmit El Niño SST and sea-level anomalies from the equator, although Simpson shows that the 1982–1983 California anomalies were more consistent with on-shore transport induced by large-scale atmospheric forcing in the north Pacific (10). In fact, the anomalies in the upwelling index in Fig. 2B, which indicate positive onshore transport anomalies, appear to propagate equatorward at 150 km day^{-1} . For several months beginning in April, upwelling indices returned to near or above normal and SST anomalies declined to 0.5° to 1.5°C. This moderation of El Niño is also evident in time series of sea level along the California coast (11) and follows a transient decline in equatorial SST anomalies that began in January and February (12).

The view of El Niño provided by these satellite images, especially the direct evidence of weakened coastal upwelling, could not be readily obtained from conventional ship and buoy data. One of the primary benefits of oceanographic sen-

sors on satellites is that they provide extensive and synoptic coverage of localized mesoscale changes at the sea surface.

PAUL C. FIEDLER

National Oceanic and Atmospheric Administration, National Marine Fisheries Service, Southwest Fisheries Center, La Jolla, California 92038

References and Notes

1. J. J. Simpson, *Trop. Ocean-Atmos. Newsl. No. 21* (1983), p. 22; R. J. Lynn, *ibid.*, p. 23.
2. J. A. McGowan, *ibid.*, p. 23.
3. *Oceanographic Monthly Summary* (available from the NOAA National Weather Service-National Earth Satellite Service, Washington, D.C.).
4. L. Lauritson, G. G. Nelson, R. W. Porto, *Natl. Oceanic Atmos. Adm. Tech. Mem. Natl. Earth Satellite Service* 107, 44 (1979); E. P. McClain, W. G. Pichel, C. C. Walton, Z. Ahmad, J. Sutton, *Adv. Space Res.* 2, 43 (1982).
5. California Cooperative Oceanic Fisheries Investigations, Cruise 8202 aboard R. V. *David Starr Jordan* by personnel of the Southwest Fisheries Center, NOAA National Marine Fisheries Service.
6. R. J. Lynn, *Geophys. Res. Lett.* 10, 1093 (1983).

7. H. R. Gordon, O. K. Clark, J. W. Brown, D. B. Brown, R. H. Evans, W. W. Broenkow, *Appl. Opt.* 22, 20 (1983).
8. Crosses in Fig. 1E mark surface pigment stations. Pigment algorithms are from R. C. Smith and K. A. Baker [*Mar. Biol.* 66, 269 (1982)] for $C_{\text{sat}} < 1.5 \text{ mg m}^{-3}$, and from (7) for $C_{\text{sat}} > 1.5 \text{ mg m}^{-3}$. The C_{sat} values on 15 March 1983 matched ship values from 17 to 18 March (all $< 0.5 \text{ mg m}^{-3}$, J. A. McGowan, Scripps Institution of Oceanography) to ± 42 percent, with a bias of +23 percent. The CZCS algorithms were less successful in matching higher ship values on 19 April 1982 (up to 8 mg m^{-3} , R. W. Owen, National Marine Fisheries Service), with a root-mean-square error of ± 66 percent and a bias of -35 percent. The biases reduce the apparent difference between 1982 and 1983 C_{sat} values.
9. J. A. McGowan, personal communication.
10. D. B. Enfield and J. S. Allen, *J. Phys. Oceanogr.* 10, 557 (1980); J. J. Simpson, *Geophys. Res. Lett.* 11, 233 (1984).
11. D. Brown, Scripps Institution of Oceanography, personal communication.
12. M. A. Cane, *Science* 222, 1189 (1983).
13. A. Bakun, *Natl. Oceanic Atmos. Adm. Tech. Rep. Natl. Mar. Fish. Service SSRF-671* (1973).
14. I thank R. Wittenberg of the Scripps Visibility Laboratory for processing the CZCS images, supported by NASA order W15, 334. I thank R. W. Owen and J. A. McGowan for providing sea-truth data, H. Orr for drafting the illustrations, and L. Prescott for typing the manuscript.

28 December 1983; accepted 27 February 1984

Ca²⁺-Dependent Protein Kinase Injection in a Photoreceptor Mimics Biophysical Effects of Associative Learning

Abstract. *Iontophoretic injection of phosphorylase kinase, a Ca²⁺-calmodulin-dependent protein kinase, increased input resistance, enhanced the long-lasting depolarization component of the light response, and reduced the early transient outward K⁺ current, I_A, and the late K⁺ currents, I_B, in type B photoreceptors of *Hermisenda crassicornis* in a Ca²⁺-dependent manner. Since behavioral and biophysical studies have shown that similar membrane changes persist after associative conditioning, these results suggest that Ca²⁺-dependent protein phosphorylation could mediate the long-term modulation of specific K⁺ channels as a step in the generation of a conditioned behavioral change.*

A learned behavioral change is acquired by the nudibranch mollusk *Hermisenda crassicornis* when trained with paired light and rotation but not with randomized stimuli (1). Biophysical changes intrinsic to the soma membrane of the type B photoreceptors have repeatedly been found only in conditioned animals during the acquisition and retention of the learned behavior. These changes, which have been implicated in the generation of conditioning in *Hermisenda*, consist of an increase in the dark membrane input resistance (R_{in}), an enhancement of the light response, notably the long-lasting depolarization (LLD) component that follows a light step (2, 3), and reduction of the early transient K⁺ current (I_A) (4). Preliminary studies suggest that other membrane currents also change with conditioning (5), as has recently been proposed (6, 7).

A number of studies taken together have suggested how these biophysical changes may occur during acquisition of the learning and how Ca²⁺ might be

involved in this process. Synaptic and light-induced depolarization of the type B cells is enhanced and more prolonged when light and rotation are paired (6). With repeated light and rotation pairings membrane depolarization persists (2, 8). Light- and voltage-dependent depolarization of the type B cell is accompanied by a rise in intracellular Ca²⁺ ($[\text{Ca}^{2+}]_i$) (9). Elevation of $[\text{Ca}^{2+}]_i$ in turn causes long-lasting inactivation of I_A (10) and possibly a Ca²⁺-activated K⁺ current (11). During retention of the conditioned response, the type B cell does not remain depolarized, but the I_A reduction persists and the LLD remains enhanced.

What biochemical process might underlie the long-term biophysical effects of conditioning, which seem to be related to elevated $[\text{Ca}^{2+}]_i$? Previously, we found that phosphorylation in a 20,000-dalton protein was altered in the eyes of conditioned animals (12) and that iontophoretic injection of the catalytic subunit of adenosine 3',5'-monophosphate (cyclic AMP)-dependent protein kinase into