We were unable to obtain permission from U.S. authorities to use the most detailed U.S. Army Map Service maps; thus, we could not resolve this question in the time available.

In Table 1 we list the archeological samples collected for comparison with the quarry results. Figure 1 shows that some success was obtained on these first "unknowns." The "Theseion" of the Athenian Agora (about 450 B.C.) is almost certainly Pentelic marble, at least on the north and south sides. The carved blocks inside the Treasury of Siphnos at Delphi are quite clearly of Parian marble. (The Treasury itself is reputed to be of Siphnian marble.) The isotopic compositions of the rest of these samples do not correspond to any of the ranges so far established for the four areas studied. It is worth noting that two quite different marbles are lying in close proximity to the Tholos (or labyrinth) of Epidaurus.

(In this connection it should be pointed out that the Athenians scatter fragments of Pentelic marble around the Parthenon each winter, in order to provide material for the insatiable pillage by tourists. This marble is from modern quarries and is isotopically distinct from that of the classical quarries. All of the samples in Table 1 are definitely ancient artifacts.)

A single sample of grey marble was collected at Caesarea, Israel, in the belief that it might be Hymettian marble imported by the Romans. However, this appears not to be the case (Table 1).

It appears that the isotopic method for determining the origin of Greek marbles will probably be the most useful of the tests so far devised, especially if used in conjunction with other techniques. Some of the archeological samples in Table 1 fall outside of the isotopic provenances so far delineated, and it is clear that other quarrying areas were used. Thus, coincidence of a sample with one of the isotopic clusters in Fig. 1 is not, in itself, a unique indication of provenance. We hope to establish a variety of geochemical characteristics of these and other marbles. We will welcome samples from areas in which other marbles used by the ancient Greeks were quarried, in order to extend the isotopic method to as many localities as possible (*16*).

HARMON CRAIG
VALERIE CRAIG
Scripps Institution of Oceanography, University of California at San Diego, La Jolla 92037

References and Notes

1. R. Lepsius, *Abh. Akad. Wiss. Berlin* (1890); H. S. Washington, *Amer. J. Archaeol.* **11**, 71 (1898).
2. G. M. A. Richter, *The Sculpture and Sculptors of the Greeks* (Yale Univ. Press, New Haven, Conn., 1950).
3. N. Herz, *Trans. N.Y. Acad. Sci. Ser. 2* **17**, 499 (1955); *Amer. J. Sci.* **253**, 299 (1955).
4. Naxian marble (the earliest quarried) could have been used in later times, but Pentelic marble is of better quality and was much more accessible to Athens. Parian marble was always in demand because of its superior luster and grain, but our studies of the underground mine from which the Lychnites marble of Paros was obtained showed that mining stopped because the unfractured Lychnites was totally removed. About 50,000 tons of this beautiful marble was ramped up two narrow shafts dipping 35° before the bed was abandoned.
5. N. Herz and W. K. Pritchett, *Amer. J. Archaeol.* **57**, 71 (1953). The geology of the Attic marbles is reviewed in this paper.
6. L. E. Weiss, *Amer. J. Sci.* **252**, 641 (1954).
7. L. Rybach and H. U. Nissen, *Radiochem. Methods Anal. Proc. Symp. 1964* **1**, 105 (1965).
8. N. Herz has pointed out to us that most of these studies simply confirm that the Greeks used the purest and most isotopic marbles that could be obtained.
9. P. Baertschi, *Schweiz. Mineral. Petrogr. Mitt.* **37**, 73 (1957); H. Craig, *Geochim. Cosmochim. Acta* **3**, 53 (1953).
10. Fieldwork was done during the fall of 1968, supported by a research grant from the University of California at San Diego. We gratefully acknowledge the many kindnesses of the following: Dr. A. Panagos of the University of Athens for many helpful discussions; Dr. E. Vanderpool of the American School of Classical Studies who led us to the Hymettian quarries; and H. Alt, F. Tsanos, and the officers of the Societé Anonyme des Carrieres du Marbre Dionyssos–Pendelis, for most helpful assistance on Mount Pentelikon.
11. A geological map of Naxos is given by I. Papastamatiou, *The Emery of Naxos* (Geological and Geophysical Surveys, Athens, 1951).
12. J. Anastopoulos, "Geological Survey of Lychnites, Paros," stencil report (Institute of Geological Subsurface Research, Athens, 1962). The name "Lychnites" refers to the lamps used underground by the ancient quarry workers.
13. The ancient quarries are on the north bank of Kakorhevma gorge, and are difficult to locate. The gorge runs east to west at the site of the quarries, which are indicated on U.S. Army Map Service Sheet NJ 34-12 (Athinai) at coordinate reference GH 4505. The Acropolis bears N67°W from the easternmost ancient quarry; the radar dome on the opposite bank is S85°E.
14. H. Craig, *Geochim. Cosmochim. Acta* **12**, 133 (1957). The PDB is a Cretaceous belemnite.
15. The ^{13}C is enriched in carbonate precipitating from solution by escape of CO_2 which is depleted in ^{13}C.
16. A great advantage of the isotopic method is that only 10 to 20 mg of $CaCO_3$ are required for both analyses. We prefer to receive larger samples in order to ensure obtaining a clean unaltered portion for analysis.
17. We thank K. Podvin and J. Brown for performing the isotopic analyses and Professor N. Herz for many helpful discussions. Dr. H. U. Nissen in Zurich was also most helpful. The laboratory work was supported by the National Science Foundation.

20 August 1971; revised 17 November 1971 ■

Electrical Conductivity and the Red Shift of Absorption in Olivine and Spinel at High Pressure

Abstract. *Above 100 kilobars the apparent absorption edges (approximately 3 electron volts) of single-crystal and polycrystalline samples of the metastable olivine and stable spinel forms of* Fe_2SiO_4 *shift rapidly with pressure from the near-ultraviolet into the lower-energy infrared region. Simultaneously, an exponential increase in electrical conductivity occurs. These effects are reversible as pressure is reduced or reapplied and are not accompanied by a first-order phase change in olivine or spinel. These observations relate to fundamental concepts of electrical conductivity and photon absorption in complex transition-metal silicates in that they cannot be readily interpreted in terms of an intrinsic band-gap model. The intensity and energy changes are too great and the effect occurs at too low a pressure to be explained by processes such as spin-pairing and other crystal-field effects. The results suggest that a new mechanism of conduction, perhaps symbiotic and employing an efficient charge-transfer process, is induced at high pressure.*

Measurements of the optical and electrical properties of fayalite (olivine, orthorhombic) and spinel (cubic) forms of Fe_2SiO_4 have been made at pressures in the range from 45 to 300 kb. The experimental apparatus is a modification of the design employed in an earlier study (*1, 2*) in which the effects described herein were first discovered. Optical absorption, electrical conductivity, and x-ray diffraction are measured simultaneously with a diamond-windowed cell in single crystals and polycrystalline powders under pressure (*3*).

Earlier definitive studies of the optical absorption properties of olivine at 1 atm (*4, 5*) dealt mostly with crystals having magnesium-rich compositions in the olivine series. High-resolution polarized spectra for iron-rich olivines at 1 atm have been reported by Burns (*6*) and Mao and Bell (*3*). Several investigators (*7*) have measured olivine spectra at high pressure, but curiously, as in the investigations of electrical conductivity mentioned below, they did not explore pressures high enough in combination with sufficiently iron-rich olivine to observe the major effects.

Properties of both natural (Inyo County, California) and pure synthetic fayalite (Fe_2SiO_4) were measured. The synthetic crystals of olivine were prepared by the repeated heating of a mixture of hematite (Fe_2O_3), metallic iron, and quartz (SiO_2) at 950°C in a container of $Ag_{80}Pd_{20}$ alloy encased in an evacuated silica glass tube. The mixture was held under a pressure of 1 kb of methane at 800°C for 3 weeks. Pure spinel crystals were synthesized by subjecting pure synthetic fayalite to conditions of 900°C and 62 kb for 1 hour in a piston-cylinder apparatus. Most of the measurements were made on polycrystalline samples, but the optical shifts were also observed in the diamond apparatus with single crystals of fayalite surrounded by a pressure medium of NaCl.

Crystal-field absorption bands of Fe^{2+} in olivine occur near 1 ev (*8*), but the spectra of interest here occur at 1 atm between 2.5 and 8 ev, depending on the iron content, and either represent the intrinsic band gap or are apparent absorption edges caused by charge-transfer processes. The latter cause intense absorption bands whose fine structure could be determined only with a thin film of sample. In our experiments polycrystalline olivine or spinel was raised to pressure in the diamond cell, and optical spectra were measured in a continuous scan of energy from the near-ultraviolet (3 ev) to the near-infrared (0.5 ev) region. Corrections for base line were obtained from numerous scans in the experimental pressure range. We compensated for chromatic aberrations by mechanically adjusting the optical system. Figure 1, A and B, shows energy scans in the range from 45 to 270 kb at 25°C for olivine and spinel. As the pressure reached approximately 100 kb or higher, the samples became brown colored and then totally opaque in the

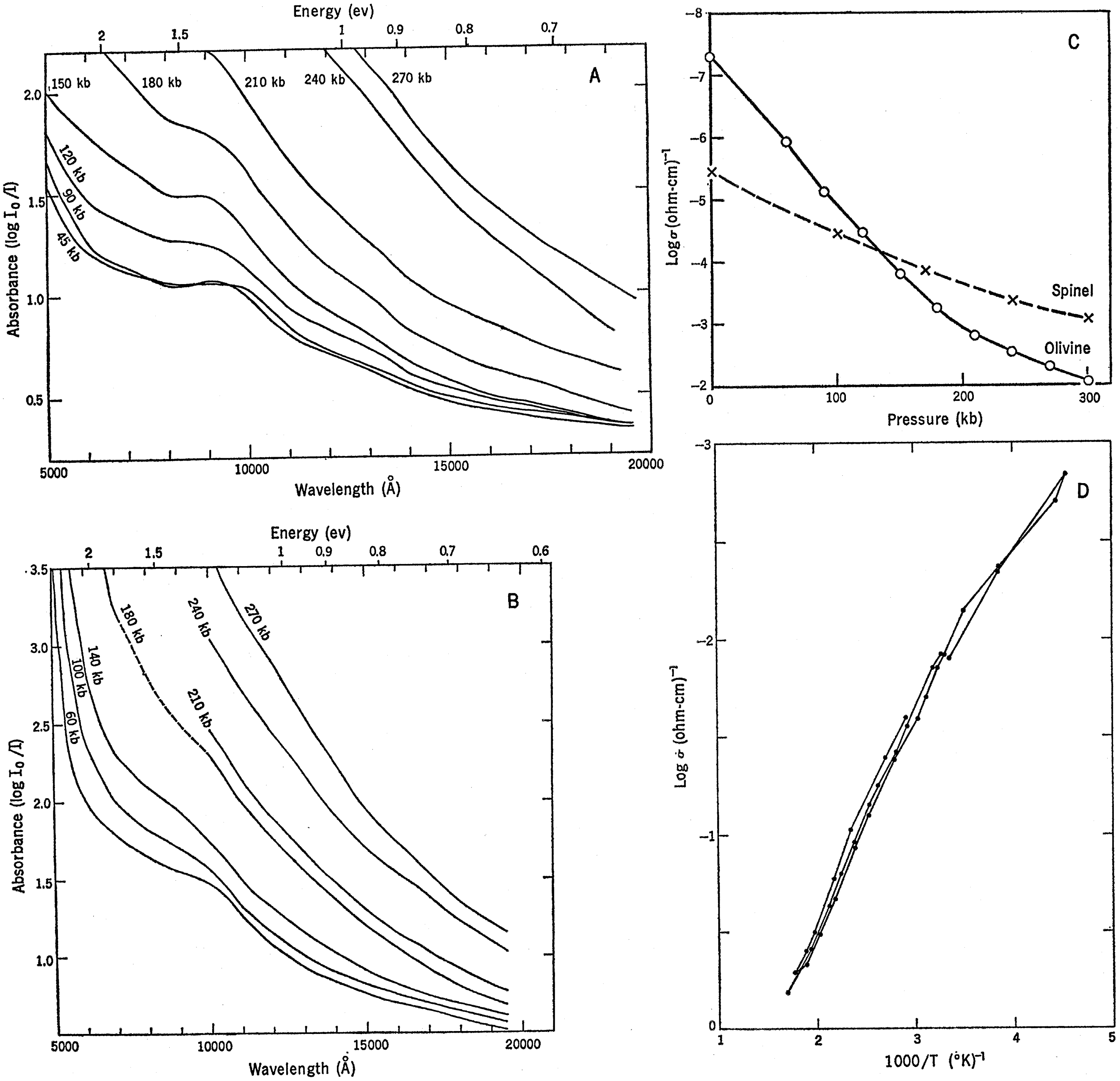

Fig. 1. (A) Absorbance (log I_0/I) of polycrystalline fayalite in the pressure range from 45 to 270 kb. (B) Absorbance of polycrystalline spinel in the pressure range from 60 to 270 kb. (C) Logarithm of the conductivity (σ) of polycrystalline olivine and spinel in the range from 1 bar to 300 kb. (D) Logarithm of the conductivity of olivine at 200 kb in the range of (1000/T) from 1.8 to 4.6.

visible region (4000 to 7000 Å). Finally, as the pressure was raised further, the broad absorption edge extended into the infrared. The effect was nearly identical in both the olivine and spinel forms. Although both phases are metastable in regions of the pressure range (fayalite is metastable above approximately 20 kb and spinel is metastable below approximately 20 kb), x-ray diffraction measurements obtained simultaneously under pressure confirm that first-order phase changes have not occurred during these experiments.

The procedures will be described in detail elsewhere (*9*), but a few words about the experimental calibrations are in order here. The pressure distribution in the diamond cell is not uniform, varying from 300 kb at the center of the cell to 1 bar at the outer portions. However, the area sampled optically is a square 50 by 50 μm in size, and here the pressure is presumed to be essentially uniform. The pressure was estimated on the basis of the torque applied to the diamonds, a technique that has been used in experiments with known standards (for example, NaCl, Fe, or AgI) in which volumes at various torques are measured at pressure by x-ray diffraction. The broad absorption could conceivably have occurred instantaneously at approximately 100 kb, and possibly not over the pressure range shown in Fig. 1, A and B, if pressure gradients occurred in the region sampled. To confirm that the effect occurs over a range of pressures, we pressurized single crystals of olivine in a matrix of NaCl. These crystals darkened in the same way as the polycrystalline samples as the pressure was increased from 100 to 300 kb. The crystals were thin (approximately 1 to 10 μm), however, and appeared to deform to a slightly increased diameter during application of pressure. Optically they appeared to remain as single crystals.

The electrical conductivity was determined by introducing fine tungsten wires (diameter before pressurizing, 0.012 mm) and measuring the resistance changes with pressure of polycrystalline samples (Fig. 2). This was done previously by Bradley *et al.* and by Akimoto and Fujisawa (*10*), but in neither investigation was the pressure high enough to permit the major effect to be observed, possibly because of equipment limitations. In our experiments the electrical conductivity was measured simultaneously with absorption and was correlated with the optical effects. As shown in Fig. 1C, the electrical conductivity in olivine increases by a factor of more than 10^5 as the process occurs. In spinel the effect is less (10^2) but still exponential. As in the case of the optical shift, there is a small probability that the increase in conductivity could have occurred more rapidly with pressure than was observed if the pressure distribution was not uniform. The curve shown in Fig. 1C is, however, remarkably reproducible from experiment to experiment, and is rapidly reversible without detectable hysteresis within an experiment.

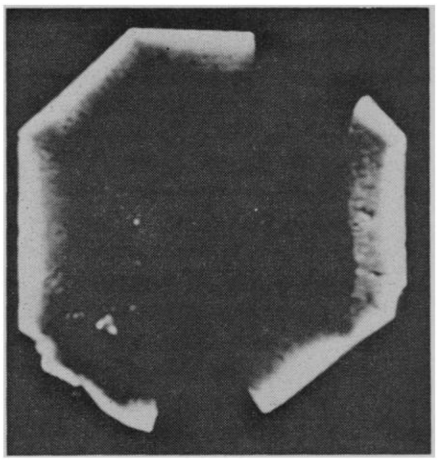

Fig. 2. Photomicrograph of polycrystalline fayalite taken through a diamond window of the pressure cell at approximately 270 kb. The wide bands on the edges are the tungsten leads used to measure electrical resistance. The geometric factors of the leads and sample within the high-pressure cell were measured optically. The pressure was greater than 100 kb in the dark area and less than 100 kb, dropping to 1 bar, in the transparent zone at the edges. The approximate dimension of the octagonal diamond face is 200 μm.

Figure 1D shows the electrical conductivity of olivine at about 200 kb. The cell was cooled with solid CO_2 and heated by varying the power of an external resistance heater. The temperature dependence is consistent with semiconductor behavior and causes a further increase in conductivity of two orders of magnitude in the temperature range studied (225° to 575°K).

The simultaneous red shift of the apparent absorption edge by a large energy change and the increase in electrical conductivity by a factor of nearly 10^6 at 300 kb are properties not characteristic of known physical mechanisms in silicates. The combined data are inconsistent with surface or impurity mechanisms, although the electrical conduction is clearly related to the iron content in olivine and spinel because the effects were not observed in pure Mg_2SiO_4. Shankland (*5*) concluded that the absorption edge at about 3 ev is not an intrinsic edge but is a band that corresponds to a charge-transfer process in Fe^{3+}. However, the observed behavior of this nonlinear feature under the present experimental conditions cannot be explained by a simple mechanism. It would require that Fe^{2+} first be oxidized and then reduced—a process that seems unlikely.

It is tempting to think that the phenomena reported here involve combined Laporte-forbidden states (*1*). Drickamer (*11*) has described the process of the closing of the band gap in insulators and semiconductors with pressure as a decrease of interatomic distance. However, a substantial compression would be required to reduce the band gap in olivine and spinel to a few units of kT (k is the Boltzmann constant, T is the temperature in degrees Kelvin). The right combination of polaron and exciton processes could provide mobilities and support transport mechanisms. The charge transfer of Fe^{2+} to Fe^{+} is known to occur in oxides (*5*), and this or another such process could support electron transport. A charge-transfer process would appear to be favored by the structural positions of the iron atoms that link silica tetrahedra (SiO_4^{4-}) in olivine (*12*). The oxidation state of iron could possibly be identified by Mössbauer resonance spectroscopy.

Both the optical and the electrical effects may be important geophysically. If olivine and spinel are abundant in the earth's mantle, one could hypothesize that heat transfer by radiation would be severely blocked at depths greater than 500 km. There is a known increase (by a factor of about 10^4) in electrical conductivity in the earth at this depth, and, if caused by pressure, this increase would significantly affect models of the earth's interior. At present, temperature profiles and components of the magnetic field in the deep mantle are calculated on the basis of the exponential Boltzmann relation between electrical conductivity and temperature. Depending on the composition and abundance of olivine and spinel in the earth's mantle, the observed effects of absorption and electrical conductivity could be used to form revised models of the thermal, electrical, and magnetic properties of the earth.

H. K. Mao
P. M. Bell
Geophysical Laboratory,
Carnegie Institution of Washington,
Washington, D.C. 20008

References and Notes

1. P. M. Bell and H. K. Mao, *Carnegie Inst. Wash. Yearb.* **68**, 253 (1970).
2. H. K. Mao, P. M. Bell, M. Raymond, *Geol. Soc. Amer. Abstr. Programs* **3**, 640 (1971).
3. H. K. Mao and P. M. Bell, *Carnegie Inst. Wash. Yearb.* **70**, 207 (1971).
4. S. P. Clark, *Amer. Mineral.* **42**, 732 (1957).
5. T. J. Shankland, *Offic. Nav. Res. Tech. Rep. HP-16* (1966).
6. R. G. Burns, *Mineralogical Applications of Crystal Field Theory* (Cambridge Univ. Press, London, 1970).
7. S. K. Runcorn, *J. Appl. Phys.* **27**, 598 (1956); A. S. Balchan and H. G. Drickamer, *ibid.* **30**, 1444 (1959); G. D. Pitt and D. C. Tozer, *Phys. Earth Planet. Interiors* **2**, 179 (1970); T. J. Shankland, *J. Geophys. Res.* **75**, 409 (1970).
8. Conversions: 10^3 nm $= 10^{-4}$ cm; 10^4 cm$^{-1} =$ 1.240 ev.
9. H. K. Mao and P. M. Bell, *Amer. Soc. Test. Mater. Spec. Tech. Publ.*, in press.
10. R. S. Bradley, A. K. Jamil, D. C. Munro, *Geochim. Cosmochim. Acta* **28**, 1664 (1964); S. Akimoto and H. Fujisawa, *J. Geophys. Res.* **70**, 443 (1965).
11. H. G. Drickamer, *Solid State Phys.* **17**, 1 (1965).
12. W. C. Bragg and G. B. Brown, *Z. Kristallogr.* **63**, 538 (1926).
13. Research supported by NSF grant GA-22707.

7 February 1972; revised 16 March 1972 ■

Deuterium Oxide: Inhibition of Calcium Release in Muscle

Abstract. *Calcium release, measured as luminescence of the protein aequorin, was measured simultaneously with membrane potential and isometric tension in single muscle fibers of the barnacle* (Balanus nubilus). *Deuterium oxide inhibited calcium release and isometric tension but did not affect membrane potential, a result consistent with the postulate that deuterium oxide inhibits the coupling between excitation and contraction.*

Deuterium oxide (D_2O) retards numerous biochemical and biological reactions (*1*, *2*). Biological effects of D_2O are due mainly to the exchange of hydrogen by deuterium at specific sites. The deuterium bond, having a lower zero-point energy, is more stable than the hydrogen bond and thus requires a greater activation energy (*3*). Some biological effects may also be related to certain differences between the solvent properties of D_2O and H_2O. For example D_2O has a higher melting point, greater density, and lower ionic conductance than does H_2O (*2*).

When the effects of D_2O on different types of muscle were studied, contraction was markedly or completely inhibited. However, even in instances of complete inhibition, the excitatory impulse continued to be propagated. In contrast, D_2O added to muscle extracted with glycerol did not retard the contraction induced by adenosine triphosphate, a result suggesting that the contractile mechanism was not influenced by D_2O. Hence, Kaminer postulated that the main inhibitory effect was on the coupling between excitation and contraction (*4*). Hotta and Morales (*5*) confirmed the lack of effect of D_2O on the contractile proteins by showing that the adenosine triphosphatase of myosin B was not influenced at neutral *p*H. Goodall (*6*) interpreted his results for living muscle as being due to the effect of D_2O on the contractile process, whereas Svensmark (*7*) remained uncertain about the site of action of D_2O. In support of Kaminer's postulate, we report evidence that calcium release, a step in the coupling of excitation and contraction (*8*), is prevented by D_2O.

Methods were similar to those of Ashley and Ridgway (*9*), who demonstrated the release of calcium in muscle by the use of aequorin, a protein which luminesces in the presence of calcium (*10*). The lateral and ventral depressor muscles of the barnacle (*Balanus nubilus*) were used (*11*). A single muscle fiber was placed in a horizontal bath in Ringer solution (*12*) buffered by 5 m*M* *N*-tris(hydroxymethyl)methyl-2-aminoethanesulfonic acid (TES) at *p*H 7.4. The experiments were done at 4°C.

After injection of 1 μl of an aequorin solution, the muscle fiber was impaled with a combination electrode for both stimulation and recording (*13*). Simultaneous measurements were made of the membrane potential, the "flash" of aequorin, and the isometric tension. After the control measurements were made, the solution was replaced with Ringer solution that contained 99.8 percent D_2O and was at the same temperature, had the same concentrations of salts, and had a *p*D equivalent to a *p*H of 7.4 (*p*D = *p*H reading + 0.4) (*14*). Recordings were then made at 5-minute intervals for 10 to 15 minutes. Figure 1 shows that the flash and the tension disappeared within 5 to 10 minutes in D_2O, while the membrane potential remained. This effect was reversed if Ringer solu-

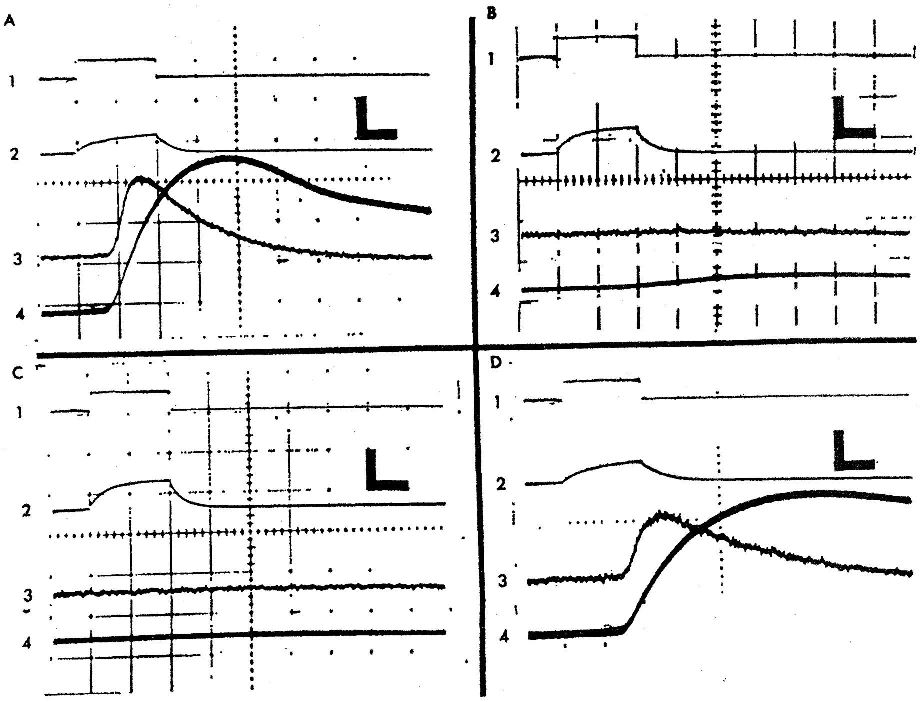

Fig. 1. Effects of 99.8 percent D_2O in a muscle fiber of *Balanus nubilis*. The control incubation (A) contained Ringer solution with H_2O. Records were made after Ringer solution with D_2O had been present for 5 minutes (B) and 10 minutes (C), and 10 minutes after the D_2O solution had been replaced with that containing H_2O (D). Traces are 1, the stimulus (45 μa, 200 msec); 2, membrane potential (20 mv/cm); 3, light emission of aequorin (1 μl of 0.1 to 0.5 m*M* aequorin was injected, and emission was measured with an RCA 6342A photomultiplier tube); and 4, isometric tension (0.5 g/cm), measured with a Grass FT03 transducer. The calibration bar equals 1 cm. After the preparation was in D_2O for 5 minutes (B) the flash disappeared; the contraction was minimal at this time and disappeared after 10 minutes in D_2O (C). There were variations in the amplitude and shape of the membrane potential. In this example, recovery is not complete; in others, recovery was complete.