5. N. S. Skorniakova, P. F. Andrushenko, L. S. Fomina, *Okeanologiya* **2**, 264 (1962).
6. J. L. Mero, *Econ. Geol.* **57**, 747 (1962); *The Mineral Resources of the Sea* (Elsevier, Amsterdam, in press).
7. K. Boström, *Geochemical Aspects of Submarine Vulcanism* (in preparation).
8. L. G. Sillén, "The physical chemistry of sea water," in *Oceangraphy*, M. Sears, Ed. (AAAS, Publ. 67, Washington, 1961)..
9. E. D. Goldberg, *J. Chem. Educ.* **35**, 116 (1958).
10. W. Buser and A. Grütter, *Schweiz. Mineral Petrog. Mitt.* **36**, 49 (1956).
11. G. Arrhenius and E. Bonatti, "Neptunism and vulcanism in the ocean," in *Progress in Oceanography* (Pettersson Volume), F. Koczy and M. Sears, Eds. (Pergamon, New York, 1964).
12. E. D. Goldberg, "Chemistry in the oceans," in *Oceanography*, M. Sears, Ed. (AAAS, Publ. 67, Washington, 1961).
13. G. Arrhenius and associates, paper in preparation.
14. E. Picciotto, "Radioactive elements and deep sea sediments," in *Oceanography*, M. Sears, Ed. (AAAS, Publ. 67, Washington, 1961).
15. S. Hietanen, *Acta Chem. Scand.* **8**, 1626 (1954).
16. G. Arrhenius, M. Bramlette, E. Picciotto, *Nature* **180**, 85 (1957).
17. J. Korkisch and G. Arrhenius, *Anal. Chem.*, in press.
18. V. M. Goldschmidt, *Geochemistry* (Clarendon Press, Oxford, 1954).
19. Supported by U.S. Atomic Energy Commission grant [AT (11-1-34] and an award from the American Chemical Society's Petroleum Research Fund (875-C6). We thank Dr. K. Boström for valuable discussion. Contribution from the Scripps Institution of Oceanography, New Series.
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X-Ray-Induced Bulk Photovoltaic Effect in Insulators

Abstract. *When an insulator, sandwiched between metals of dissimilar work functions, is irradiated with x-radiation, a voltage related to the contact potential difference of the metals is observed. This phenomenon, known as the bulk photovoltaic effect, has been demonstrated in a variety of metal-insulator-metal combinations. Evidence that the voltage is not generated by junctions, barrier layers, or similar other phenomena is presented.*

The bulk photovoltaic effect in insulators, previously described theoretically by Tauc (*1*), has heretofore been demonstrated experimentally only with visible and ultraviolet light (*2*).

One type of cell which displays the bulk photovoltaic effect consists of an insulator between, and in intimate contact with, two metals of different work functions. The contact potential difference between these metals appears as a voltage across the insulator when the metals are connected through an external resistance. The resulting electric field in the insulator will accelerate any current carriers raised into the conduction band. We have studied cells in which the energy needed to excite current carriers is provided by ionizing radiation—50 kv (peak) x-rays—absorbed in the insulator. In this case, part of the energy lost by radiation in the insulator is delivered to carriers raised to the conduction band and is thus made available to do work in an external circuit. This effect is fundamentally different from the better known "barrier-layer photovoltaic effect" which is observed only in true semiconductors and depends for its voltage upon a depletion region due to a *p-n* junction. (See *1* for a discussion of the distinction between these two phenomena.)

Cells which display the bulk photovoltaic effect under the beam from a 50-kv x-ray tube have been fabricated from a variety of insulators in different thicknesses and with different pairs of electrode metals. The combinations in which we have observed the effect are listed in Table 1.

The cells enumerated in Table 1 gave open-circuit (10^{11} ohm electrometer load) voltages ranging from 0.15 for the CdS (with In, Au) up to 1.85 for the anodized Al_2O_3 between Al, Au. The insulator thicknesses much greater than 10^{-4} cm gave short-circuit currents which were orders of magnitude lower than the thinner insulators made by anodizing, as might be expected owing to carrier recombination and trapping. By far the highest output was obtained from the thickest achievable Ta:anodized Ta_2O_5:Au cells, which gave up to 5 μa short-circuit current when irradiated with 50-kv x-rays (tube current was 44 ma). The response of typical Ta:anodized Ta_2O_5:Au cells is shown in Fig. 1. Of particular interest are the open-circuit voltages (the highest value of voltage) and the short-circuit currents (at the intersection with the horizontal axis).

Two "null" cells were fabricated to demonstrate that the voltage observed was not generated by junctions or some other phenomenon within the insulator. (i) A cell of Al:anodized Al_2O_3:Al was prepared on the same anodized Al block as a cell of Al:anodized Al_2O_3:Au. Under x-irradiation this Al:Al cell gave an open-circuit voltage of less than 0.050 compared to 1.85 for the Al:Au cell on the same oxide layer. (ii) A cell of Ta:anodized Ta_2O_5:Al was prepared which gave an open-circuit voltage of only 0.2 compared to all other Ta:anodized Ta_2O_5 cells using either Au or Ag, which gave voltages in excess of 0.95. Since the work function difference of Ta:Al is about 0.1 volt (much lower than the Ta:Au or Ta:Ag differences which approach 1 volt), this qualitatively constitutes a null experiment.

These null cells demonstrate that the cell voltage depends on the existence of a large contact potential difference between the electrode metals.

To demonstrate that the phenomenon is not due to a depletion region (barrier) near one electrode, cells of Ta:anodized Ta_2O_5:Au were prepared with the oxide layers of different thicknesses ranging from 0.1 to 3.5 μ. The short-circuit photocurrents from cells with oxide 2.2 and 3.5 μ thick (thickness measured by metallurgical sectioning) were directly proportional to the oxide thickness, thus showing that carrier collection is a bulk effect.

Some of the cells which gave high output under the x-ray beam were ex-

Table 1. Metal-insulator-metal combinations in which the x-ray induced bulk photovoltaic effect has been demonstrated. The first-named electrode metal is a substrate upon which the insulator was deposited; the last (more noble) metal was evaporated in vacuum (except for the Al: sulfur: Pt cell).

Insulator	Insulator thickness (cm)
Al,Au electrode	
Al_2O_3 (anodized)	10^{-5}, 3×10^{-5}
Al_2O_3 (sapphire)	3×10^{-2}
$CdWO_4$ (crystal)	7×10^{-2}
$CaWo_4$ (crystal)	3×10^{-2}
Mylar film	10^{-3}, 3×10^{-3}
Ta,Au electrode	
Ta_2O_5 (anodized)	10^{-5} to 10^{-4}
Silicone varnish	$\backsim 10^{-3}$
Ta,Ag electrode	
Ta_2O_5 (anodized)	7×10^{-5}
Al,Pt electrode	
Sulfur (cast)	1.5×10^{-2}
In,Au electrode	
CdS (10^{12} ohm-cm crystal)	8×10^{-3}
Ta,Al electrode	
Ta_2O_5 (anodized)	7×10^{-5}
Ta,Pt electrode	
Ta_2O_5 (anodized)	10^{-4}

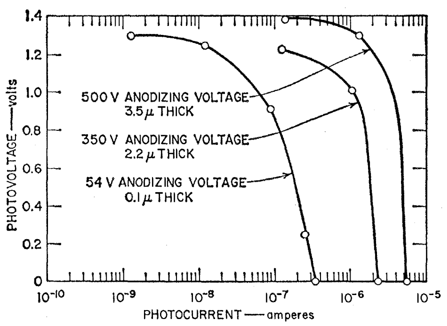

Fig. 1. X-ray induced bulk photovoltaic effect in cells of Ta_2O_5 with Ta and Au electrodes.

posed to ultraviolet irradiation, γ-ray irradiation (from a 1.2-kc Co^{60} source), Sr^{90} irradiation (from a 50-mc source), and 1-Mev electron beam irradiation. All of these irradiations gave an observable bulk photovoltaic effect appropriate to the radiation dose rate.

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References and Notes

1. J. Tauc, *Rev. Mod. Phys.* **29**, 318 (1957).
2. W. C. van Geel *et al.*, *Philips Res. Rept.* **13**, 265 (1958).
3. Supported by Stanford Research Institute funds managed by the SRI Physical Sciences Research Committee.

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Polar Transport of Calcium in The Primary Root of Zea mays

Abstract. *Transport of calcium-45 in 20-mm root segments is basipetal and requires metabolic maintenance. Such transport reaches a maximum rate after immersion of the roots in tracer solution for approximately 12 hours and is still pronounced after 50 hours. Acropetal movement is slight, probably non-metabolic, and essentially constant. Amounts transported are linearly dependent on the absorbing area exposed to tracer solution.*

Ion absorption and translocation in plants has long been known to be a complex sequence of events which can be influenced by transpirational flow. It is generally agreed that the actual absorption of ions is predominantly metabolic while their subsequent upward movement with the transpirational stream is passive. The need for more experiments designed to investigate the catenary nature of this absorption-translocation process has recently been emphasized (*1*). A newly developed method (*2*) of sealing short root segments between two compartments without damaging the roots now makes such an investigation possible. Preliminary results which demonstrate the directional and metabolically mediated transport of calcium in the absence of transpirational flow are summarized in this report.

Zea mays L. var. Peoria was grown in the dark in 0.25 m*M* calcium nitrate solution at 25°C after the manner of Handley, Vidal, and Overstreet (*3*). Characteristically, the roots did not develop root hairs (*4*). Segments 20 mm in length were cut from the primary root of 4-day-old seedlings and sealed into small glass tubes (called root chambers; 1.5-ml volume) as shown in Fig. 1. The seal was effected by compressing a Parafilm-M gasket against the bottom of the root chamber thus forcing some of the sealing compound (5 percent paraffin and 95 percent lanolin) into the bevelled capillary. The segments used were cut at 10 and 30 mm from the apex so that both the apical meristem and the region of elongation were excised (Fig. 1). The segments, therefore, did not elongate during an experiment and presented a cut surface to both solutions regardless of orientation. Because fully differentiated xylem may not always be found in the region 10 to 15 mm from the apex (Fig. 1) (*5*), segments cut from 20 to 40 mm were also tested for orientation-dependent transport of tracer. Both the 10- to 30-mm and the 20- to 40-mm segments showed a pronounced orientation effect (Table 1); therefore, differences in xylem differentiation do not appear to be the basis for the polarity reported here.

Calcium-45 (0.05 μc/ml) was used as the tracer in a solution containing 5 meq/liter of $CaCl_2$ at *p*H 6.3 ± 0.5. The root segments were immersed in 200 ml of aerated tracer solution until the surface of the solution just contacted the base of the pressure seal. Movement of tracer into the root chamber, which usually contained distilled water, was determined by withdrawing and replacing the chamber solution at 3-hour intervals. The solutions from the root chambers of three similarly oriented root segments were combined, evaporated to dryness, taken up in acidified toluene-ethanol liquid scintillant (*6*), and counted at an efficiency of 54 percent with a liquid scintillation spectrometer.

Movement of calcium in oppositely oriented root segments (10 to 30 mm) showed a pronounced polarity—that is, preferential basipetal transport (Fig. 2). The maximum basipetal transport increment occurred aproximately 12 hours after the segments were immersed in the tracer solution, at which time the basipetal increment was more than 20 times the acropetal increment. After 50 hours the two increments still differed by a factor greater than five. The gradual decline in transport after 12 hours was probably a reflection of a lower metabolic rate resulting from the depletion of respiratory substrate. This polar movement presumably occurred in the absence of transpirational flow, and against both a 5-cm hydrostatic pressure and an osmotic gradient of approximately 0.2 atmospheres. With a 5 meq/liter solution of $CaCl_2$ in the root chamber, the observed incremental transport of Ca^{45} is not statistically different ($p < .01$) from that presented in Fig. 2. The total amount of Ca^{45} retained by the root segments showed no statistically significant differ-

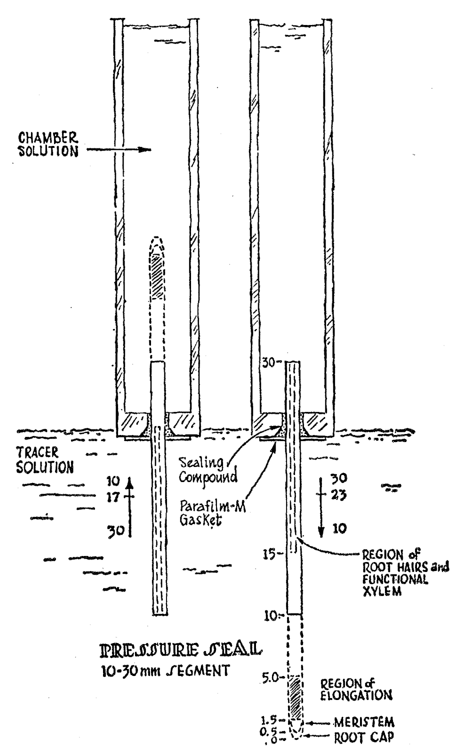

Fig. 1. Cross section of the pressure seal showing the root chamber with sealed 10 to 30-mm root segments in place. Positions of the various regions of *Zea mays* root in relation to the seal are also given. Symbols indicating sealing position (arrows with distance in millimeters to apex) are shown beside the root segments.