Pliocene boundary problem is the decision as to its definition. I have suggested that it be recognized by the first abundant appearance of *Sphaeroidinella dehiscens dehiscens* in geologic time (the *Sphaeroidinella dehiscens* datum) (*6*, *8*). It is quite arbitrary to do this; some investigators might prefer to place the base of the Pliocene at the base of the Pontian, or in a higher position than that preferred herein; this is a problem which is beyond the scope of this discussion. The important problem here is the magnitude of the unconformity separating the Pleistocene sediment veneer from the underlying later Miocene sediment in the deep-sea cores of Ericson *et al.* (*1*), an unconformity representing a time gap of some 10 to 12 million years, the approximate duration of the Pliocene. In the Philippines, a thick section of hundreds of meters of Lower Pliocene strata rest above the equivalent zone recognized below the boundary in the deep-sea cores.

Reworking of Miocene, or older, assemblages into Pliocene, Pleistocene, and Recent sediments is always a possible way of explaining faunal mixtures; the case of the deep-sea cores does not seem to be explainable in this way (*11*).

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Phosphate Glass Electrode with Good Selectivity for Alkaline-Earth Cations

Abstract. *A phosphate glass has been found to have a significant electrode specificity toward alkaline-earth ions. The order of selectivity is* $2H^+ > Ba^{++} > Sr^{++} > Ca^{++} > 2K^+ > 2Na^+ > Mg^{++}$. *Exchange properties are discussed in relation to possible structure. Its use to determine activity of* Ca^{++} *in natural systems containing* Mg^{++} *is suggested.*

The ion-exchange selectivity of glasses can be studied through their behavior as membrane electrodes (*1*); conversely conclusions may be drawn from the ion-exchange behavior of a material to predict its electrode response. Some silicate minerals exhibit pronounced selectivity toward alkali cations, especially clays (*2*) and feldspars (*3*) for the larger ions. On the other hand, minerals having pronounced selectivity for alkaline-earth cations are mostly phosphates (*4*). There are exceptions to this generalization: silicate glasses can have an alkaline-earth response (*5*) and phosphates with alkali-cation selectivity are known (*6*). Still, it is evident that phosphate glasses are likely to exhibit good selectivity toward alkaline-earth cations.

Silicate glass electrodes sensitive to alkaline-earth cations (*5*) have a calcium-magnesium selectivity ratio not high enough for use in the determination of calcium activity in the presence of magnesium; this is a definite limitation, because many natural systems contain magnesium. Such electrodes are also sensitive to alkali cations and hydrogen ions, but this is not serious because electrodes sensitive to these ions are available (*7*) and corrections can be made if the activities of the ions are known. Analog computers for such corrections have been reported (*8*) and the necessity for measurement of interfering ions, if calcium activities are to be determined, has been discussed (*9*). Some phosphate glasses have been used as alkali-ion electrodes (*10*). These glasses contain Na, Ca, P, and O, and have very high electrical resistance and poor durability, but their sensitivity to alkaline-earth cations has not been reported.

A piece of phosphate glass prepared for radioactive waste disposal studies (*11*) was available, and we tested its membrane electrode behavior. This glass was prepared at Brookhaven National Laboratories (*12*) by heating a synthetic nonradioactive analog of Purex waste, which is a material derived from stripping fission products from spent reactor elements by strong acids (*13*), in the presence of phosphoric acid. Initial evaporation and denitration was carried out at 120°C until most of the nitric acid was removed; the mixture was then heated to about 300°C until the rest of the nitric acid and most of the sulfuric acid present were removed; the reaction product then was heated to 1000°C and held at this temperature until all sulfates had been removed, and then cooled (*11*). It appeared almost black and was free of bubbles.

Chemical analysis of the glass showed, in percent by weight: SiO_2, 3.1; Al_2O_3, 5.6; total iron as Fe_2O_3, 16.0; Na_2O, 6.1; K_2O, 0.09; H_2O, 0.19; and P_2O_5, 66.7 (*14*). This indicated that one part of phosphoric acid had been added to four parts of synthetic Purex solution. The results of spectrographic analysis of the glass are given in Table 1.

We can assume that this glass is a network structure, but with some oxygens bonded only to one phosphorus (in a phosphate tetrahedron), the remaining charge on these oxygens being balanced by Na^+, because (excluding Na which is octahedrally coordinated) the oxygen-to-metal ratio, as computed from the chemical analysis, is 2.3:1, intermediate between that of a three-dimensional network (2:1) and an

Table 1. Spectrographic analysis of the phosphate glass. These results are reported in percentage to the nearest number in the series 1, 0.7, 0.5, 0.3, 0.2, 0.15, 0.1 and so forth; these numbers represent approximate midpoints of group data on a geometric scale. The assigned group for semiquantitative results includes the quantitative value about 30 percent of the time. *M* denotes "major constituent."

Element*	%	Element	%
Si	1	Cr	0.3
Al	3	Cu	.002
Fe	*M*	Ga	.001
Mg	0.015	La	.015
Ca	.2	Mo	.07
Na	> 5.6	Ni	.2
Ti	0.3	Sc	.0003
P	*M*	Sr	.01
Mn	0.03	V	.001
B	.0015	Y	.03
Ce	.01	Yb	.0005
Co	.0007	Zr	.03
Ba	.003	Nd	.02

* Looked for, but not detected, K, Ag, As, Au, Be, Bi, Cd, Ge, Hf, Hg, In, Li, Nb, Pb, Pd, Pt, Re, Sb, Sn, Ta, Te, Th, Tl, U, W, Zn, Pr, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Lu, Ru, Cs.

infinite-sheet structure (3:1). It is an ultraphosphate glass (*15*).

Table 2. Values of K_{AB} for the phosphate glass.

Ion A	Ion B						
	[H^+]	[Na^+]	[K^+]	[Mg^{++}]	[Ca^{++}]	[Sr^{++}]	[Ba^{++}]
[H^+]	1.0*	4.5×10^{-4}*	6.6×10^{-4}*	1.5×10^{-4}†	7.9×10^{-4}†	2.6×10^{-3}†	9.1×10^{-3}†
[Na^+]		1.0*	1.48*	0.34†	1.78†	5.9†	20.4†
[K^+]			1.0 *	0.23†	1.20†	4.0†	13.8†
[Mg^{++}]				1.0 ‡	5.23‡	17.4‡	60 ‡
[Ca^{++}]					1.0 ‡	3.3‡	11.5‡
[Sr^{++}]						1.0‡	3.5‡
[Ba^{++}]							1.0‡

* K_{AB}; Eqs. 1 and 1a apply. † K_{AB}; Eqs. 2 and 2a apply. ‡ K_{AB}; Eqs. 3 and 3a apply.

Membrane electrodes of the phosphate glass were prepared by cementing a thin section (0.1–0.2 mm) of the glass to the end of a strong glass tube, filling the tube with dilute HCl and inserting Ag-AgCl wire (*1*). The phosphate glass was not as durable chemically as silicate glasses previously used, and it had slightly higher conductivity.

The electrode was strongly affected by prior conditioning in regard to its electrical resistance and speed of response. The response of some electrodes was so slow that an exchange titration took as much as 10 hours to complete. The titration procedure was as described (*1*), except that, whenever a specific cation electrode (*7*) was available, it was used to measure that cation's activity directly, rather than calculating it from the molality and activity coefficient.

The experimental results of the electrode behavior of this glass confirm the predicted response to alkaline-earth cations. The phosphate glass (exchange constants given in Table 2) shows greater selectivity for the larger divalent cations and for divalent compared to monovalent cations (except H^+) than any silicate glass thus far reported. The constants given are for these equations (A and B are cations, X an exchange site, and brackets denote activities):

$$A_2X_2 + 2B^+ = B_2X_2 + 2A^+ \tag{1}$$

$$K_{AB} = \frac{[A^+]^2[B_2X_2]}{[B^+]^2[A_2X_2]} \tag{1a}$$

$$A_2X_2 + B^{++} = BX_2 + 2A^+ \tag{2}$$

$$K_{AB} = \frac{[A^+]^2[BX_2]}{[B^{++}][A_2X_2]} \tag{2a}$$

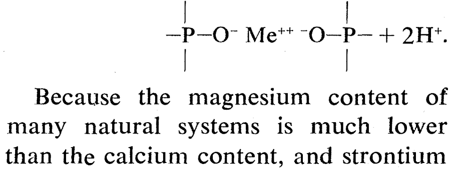
$$AX_2 + B^{++} = BX_2 + A^{++} \tag{3}$$

$$K_{AB} = \frac{[A^{++}][BX_2]}{[B^{++}][AX_2]} \tag{3a}$$

The corresponding electrode equations have been published (*1*) and the significance of K_{AB} is the same here.

Eisenman has stated that the order of alkali ion specificity in electrode glasses depends only on the anionic field strength of the glass (*16*). This is so because the differences in the electronegativity of the oxygen atoms in various glasses depend on the character of the adjacent electropositive atoms (P, Si, Al, Fe) and the local structure and can be represented by different values of the equivalent anionic radius or anionic field strength. It has been pointed out (*17*) that for divalent cations, specificity also depends on site-to-site distance. Truesdell (*18*) has extended Eisenman's theory to divalent cations and has shown the relation between alkaline-earth cation selectivity of silicate glasses, the anionic field strength (as expressed by the equivalent anion radius), and the site separation.

Eisenman (*10*) estimates that an oxygen of an isolated phosphate tetrahedron would have an equivalent anion radius of 1.4 Å, and an unshared (not shared between phosphate tetrahedra) oxygen of a polyphosphate group will have a larger equivalent anion radius. The separation of sites formed by unshared oxygen atoms of adjacent phosphate tetrahedra is approximately 5 Å, but since nearly half of the tetrahedra have entirely shared oxygen atoms, there is no simple way to calculate true site separation. At a site separation of 4 Å or greater, and with an equivalent anionic radius of $>$ 1.4 Å, the order of exchange selectivity among the divalent ions may be calculated (*18*) as $Ba^{++} > Sr^{++} > Ca^{++} > Mg^{++}$. This order is in fact observed. The divalent-monovalent selectivity is much greater, however, than that predicted. The composition of the surface of the glass, in which exchange takes place, may be quite different from the bulk glass because it becomes hydrated during conditioning. A divalent ion and a water molecule might react with a shared oxygen to give two unshared oxygens producing paired sites with a separation determined by the size of the divalent ion:



$$-P-O-P- + Me^{++} + H_2O = -P-O^- \; Me^{++} \; {}^-O-P- + 2H^+.$$

Because the magnesium content of many natural systems is much lower than the calcium content, and strontium and barium are usually not present in significant amounts, it is likely that phosphate glasses can be used to determine calcium activity in such systems. If the Mg content is high, measurements with both a phosphate and a silicate glass electrode with alkaline-earth cation sensitivity (*5*) may be useful. Because the phosphate glass electrode is *p*H-sensitive and responds to alkali cations, Na^+ and K^+ activities may have to be determined with suitable glass electrodes, and the *p*H must be known and should not be less than 6. The long time necessary for conditioning the electrode (up to 4 hours), its fragility, and its high electrical resistance, which makes necessary the use of a high impedance electrometer, are serious drawbacks which make it likely that this electrode is practical only if calcium activities must be known—even at the price of considerable inconvenience. A previous method for determining calcium activities utilizing frog heart contractions (*19*) has not become popular because of its inconvenience. The electrode method, at the present time, is also quite tedious.

Although the phosphate glass electrode in its present state of development is not a suitable substitute for established methods for determining Ca and Mg, previous work with Na^+ electrodes has established their value in supplementing (*9, 20*) conventional Na determinations and it appears that divalent glasses with more favorable mechanical and electrical properties may become available in the future. In this connection, it is appropriate to recall the words of Neuman and Neuman, "whoever develops a simple accurate method for the estimation of calcium ion activities will truly be a hero to clinician and researcher alike" (*21*; *22*).

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Diurnal Rhythm and Photoperiodism in Testicular Recrudescence of the House Finch

Abstract. *A circadian rhythm in house finches appears to control the timing of the photoperiodic response of testicular recrudescence. A 6-hour light period coupled with dark periods of varying duration does not stimulate spermatogenesis in cycle lengths of 24, 48, and 72 hours, but initiates spermatogenesis in cycles of 12, 36, and 60 hours.*

It is well established that the photoperiod influences the reproductive cycle of birds in temperate zones (*1*). Since the discovery of the avian photoperiodic response by Rowan (*2*) in 1925, many investigators have sought to explain how birds make the critical distinction between long days and short days. Rowan himself thought that the increasing length of the day in spring was the important factor. Later investigators postulated that the absolute length of the light period is critical (*3*); some believed that the light period is rate limiting but with a "carry-over period" into the darkness (*1*). Others postulated that there is a dark-dependent phase (*4*), and some believed that darkness has an inhibitory role (*5*). Another hypothesis (*6*), originally advanced to explain the photoperiodic mechanisms of plants, has since been extended to animals (*7*) and postulates that an endogenous diurnal rhythm is involved in the photoperiodic response. Experiments have been performed for the specific purpose of testing this hypothesis in animals (*8*), but the evidence for all those hypotheses still is subject to controversy. The experiments described in this paper were designed to test the endogenous rhythm hypothesis by utilizing a technique that has proved useful in examining the photoperiodic responses of short-day plants (*9*).

Table 1. The stages of spermatogenesis in testes of birds in experiment 1 (x) and experiment 2 (o). Stage I, spermatogonia only; stage VI, many sperm in tubules.

Stage	6L/6D	6L/18D	6L/30D	6L/42D	6L/54D	6L/66D
VI	ooooo		o			
V	xxxxo		xxoo		xo	
IV	x		xoo		x	
III					xxx	
II					ooo	o
I		xxxxxxo		xooooo		xxxxooooo

Adult house finches, *Carpodacus mexicanus*, a common nonmigratory fringillid of western North America, were trapped in the vicinity of this university and placed in groups of 10 (experiment 1) and 6 (experiment 2) in cages measuring approximately 70 × 30 × 30 cm. Commercial canary seed, water, and gravel were available at all times, and fresh fruit was supplied once a week. The cages were placed in the open drawers of "photocyclers" (*10*) and all were exposed to the same intensity of light (4400 to 11,000 lu/m^2) from GE Cool White fluorescent tubes. When the drawers were closed the cages were in complete darkness. The temperature varied from 24° to 32°C.

All the birds in both experiments were given a similar preliminary treatment. For 2 months they were subjected to short days of 6 hours light and 18 hours darkness (6L/18D). After this 2-month period, some of the birds, selected at random from the stock, were placed on long-days (18L/6D) for 25 days. These birds responded positively by showing complete testicular recrudescence. The testes of four birds castrated before both experiments served as preexperimental controls; their testes were all in an immature condition. The experimental birds subjected to a 6L/18D schedule (identical to the initial 2-month treatment) served as short-day controls. In both experiments a 6-hour light period was coupled with a variety of dark periods to give cycles of 12, 24, 36, 48, 60, and 72 hours.

In experiment 1, the surviving finches were killed with chloroform after 33 days; the left testis was removed, weighed, and preserved in Bouin's solution. The testes were sectioned at 10μ and stained with Harris' haematoxylin and eosin. In experiment 2, the birds were assayed after 22 cycles of treatment (except that the birds subjected to the 6L/6D regimen received 44 cycles). These birds were anesthetized, unilaterally castrated, and subsequently released. The left testis was weighed, preserved, sectioned, and stained as above. The degree of spermatogenesis in both experiments was categorized after Bartholomew (*11*).

Data on the weight of the testes of birds in both experiments are presented in Fig. 1. Enlargement and maturation of the testes did not occur in the house