foods, the use of ozone in concentrations of 1 to 3 ppm has been recommended (*2*). The results obtained with glass containers indicate that the ozone concentrations found might be of significance from the standpoint of inhibiting microbial growth. Although rapidly dissipated in the presence of organic matter, ozone is continuously replenished during irradiation. Thus ozone might have possibly contributed to the microbial inhibition observed with foods irradiated in air or in packages containing some air. One may also wonder if some of the detrimental effects of radiations on foods, particularly on flavor, might have resulted from the ozone formed during irradiation.

Many plants, including tomatoes, Pinto beans, spinach, and potato, are sensitive to ozone at concentrations below 0.1 ppm (*4*). Lettuce leaves, after irradiation, develop epidermal lesions (freckles) consisting of rust-colored spots, mostly on the midvein; when irradiated in nitrogen the spots do not appear (*11*). We were able to produce these spots by exposing lettuce leaves to the irradiated air from which we obtained the results shown in Table 1. But when lettuce leaves were irradiated in the presence of activated charcoal, the spots did not appear. These results indicate that ozone might cause the development of "freckles." Thus, "radiation injury" to plants might sometimes be due to the ozone.

Finally, the public health aspect of these findings should not be overlooked. The ozone concentrations which can be detected by odor and the concentrations which may have harmful effects have not been firmly established. The maximum allowable concentration established by the American Council of Governmental and Industrial Hygienists (*12*) is 0.1 ppm ozone in air, although different concentrations have been reported by others (*2, 13*). Breathing air containing 0.1 ppm ozone may cause respiratory discomfort, headaches, depression, and other undesirable symptoms (*12*). It would seem that for continued exposure, especially when more powerful radiation sources are used, the health hazards from ozone should be taken into consideration. (*14*).

Z. I. KERTESZ*
GRACE F. PARSONS

New York State Agricultural
Experiment Station, Cornell
University, Geneva

References and Notes

1. U.S. Army Quartermaster Corps, *Radiation Preservation of Food* (U.S. Government Printing Office, Washington, D.C., 1957).
2. V. A. Hann and T. C. Manley, in *Interscience Encyclopedia of Chemical Technology,* (Interscience, New York, 1952), vol. 9, pp. 735–753; W. C. Frazier, *Food Microbiology* (McGraw-Hill, New York, 1958); F. W. Tanner, *The Microbiology of Foods* (Garrard, Champaign, Ill., ed. 2, 1944).
3. C. Homan, *Plant Physiol.* **12**, 927 (1937).
4. M. C. Ledbetter, P. W. Zimmerman, A. E. Hitchcock, *Contrib. Boyce Thompson Inst.* **20**, 275 (1959); S. M. Siegel, *Plant Physiol.* **37**, 261 (1962).
5. R. S. Hannan, *Scientific and Technological Problems Involved in Using Ionizing Radiations for the Preservation of Food* (Her Majesty's Stationery Office, London, 1955).
6. N. W. Desrosier and H. M. Rosenstock, *Radiation Technology in Food, Agriculture and Biology* (Avi, Westport, Conn., 1960); D. K. Salunkhe, *Econ. Botany* **15**, 28 (1961); W. M. Urbain, *J. Agr. Food Chem.* **8**, 340 (1961).
7. W. Deckert, *Z. Anal. Chem.* **153**, 189 (1956).
8. C. E. Thorp, *Ind. Eng. Chem.* **12**, 209 (1940); B. E. Saltzman and N. Gilbert, *Anal. Chem.* **31**, 1914 (1959).
9. M. S. Egorow, *Z. Untersuch Lebensm.* **56**, 355 (1928).
10. See on this point S. C. Lind, *Radiation Chemistry of Gases* (Reinhold, New York, 1961).
11. Z. I. Kertesz *et al.*, *A Study of the Radiation Induced Softening of Plant Tissues, Final Rept., Contract DA-19-129-QM-1584* (Office of Technical Services, U.S. Dept. of Commerce, Washington, D.C., 1962).
12. N. I. Sax, *Dangerous Properties of Industrial Materials* (Reinhold, New York, 1957).
13. A. W. Ewell, *Ice and Refrig.* **120**, 55 (1951); W. Witheridge and C. Yaglon, *J. Am. Soc. Heating Ventilating Engrs.* **45**, 509 (1939).
14. Approved by the director of the New York State Agricultural Experiment Station, Geneva, as Journal Paper 1277, 28 August 1961. This investigation was supported in part by U.S. Public Health Service grant A2367 from the National Institute of Arthritis and Metabolic Diseases.

* Present address: Nutrition Division, Food and Agriculture Organization of the United Nations, Rome, Italy.

19 August 1963 ■

Miocene-Pliocene Boundary in the Philippines as Related to Late Tertiary Stratigraphy of Deep-Sea Sediments

Abstract. *Planktonic foraminiferal trends across the Miocene-Pliocene boundary in the Philippines suggest that sections of eight deep-sea cores reported to be Pliocene are actually latest Miocene, and that a marked extinction of discoasters in the deep-sea cores is due to an unconformity, separating Miocene and Pleistocene sediments, representing a time gap of some 10 million years of Pliocene time.*

Recently, a "Pliocene-Pleistocene" boundary was defined by various paleontological criteria in seven deep-sea cores from the Atlantic Ocean and one in the Indian Ocean, all apparently from submarine rises, by Ericson, Ewing, and Wollin (*1*). Riedel, Bramlette, and Parker (*2*) have questioned the position of the boundary as representing the Pliocene-Pleistocene boundary. The eight cores were selected specifically because the Pleistocene sediment blanket was thin, probably owing to loss of sediments by slumping or submarine erosion, or to the nondeposition of sediments; thus, it was possible for the core barrel to penetrate through the Pleistocene into older sediments beneath. I have found planktonic foraminiferal trends in sections (*3*), deep water in origin, of the Philippines (Fig. 1) that indicate the "Pliocene-Pleistocene" boundary in the eight deep-sea cores is a Miocene-Pleistocene boundary, and suggesting that some 10 million years of sediment deposition is absent at the boundary in the deep-sea cores of Ericson *et al.* The deep-water origin of the Philippine section is based upon deep-water benthic foraminifera such as *Bulimina rostrata, Nonion pompilioides, Pyrgo serrata,* and *Uvigerina hispida,* all of which have modern representatives in deep bathyal areas of modern oceans.

Ericson, Ewing, and Wollin gave six criteria for defining the boundary in their cores. First, a prominent extinction of discoasters occurs at the boundary. It has been pointed out by Riedel *et al.* (*2*) that there has been a gradual decline of discoasters since the Middle Miocene; thus, an unconformity representing a gap of many millions of years would result in abundant discoasters below such a boundary and few if any above the boundary. Second, a change occurs in the coiling direction of *Globorotalia menardii* from 95 percent dextral, or right-coiling, below the boundary to 95 percent sinistral, or left-coiling, above the boundary in the Pleistocene. Such a change occurs in the Philippine sections (Fig. 1) from dominantly dextral specimens of *G. menardii* in the uppermost Miocene to mostly sinistral specimens in the lower part of the Pliocene, as defined in that area; hence, dextral Miocene populations below sinistral Pleistocene populations would be expected. Third, *Globorotalia truncatulinoides* appears in abundance above the boundary in the deep-sea cores in the Pleistocene sediments and they report it as absent in the "Pliocene" sections of deep-sea cores. This species is abundant and quite representative throughout deep-water marine beds of the Pliocene in the Philippines; it is reported in the Pliocene of Italy (*4*) and Venezuela (*5*); therefore, it is quite logical to expect it to be absent from the deep-sea core sediments below the boundary if those sediments are not Pliocene but later Miocene in age. Fourth, *Globigerinoides triloba sacculifera* is within the core segments below the lower Pleistocene boundary; however, this species first appears in latest Miocene time and ranges through the Pliocene (Fig. 1), so its presence is not unusual or unexpected in the sediments below the boundary in the eight deep-sea cores. Fifth, a reduction of the *G. menardii* complex to a single fairly uniform race above the boundary would be expectably dramatic by telescoping the Miocene populations against Pleistocene assemblages. Sixth, an increase in the diameter of *G. menardii* would prevail whether one compares the Pliocene or the Miocene populations with those of the colder water assemblages.

A second aspect of the deep-sea cores of Ericson *et al.* (*1*) is the sequence of typical Miocene planktonic foraminifera in the core segments they referred to as Pliocene; these segments are below my *Sphaeroidinella dehiscens* datum (*6*). There is the same sequence of planktonic species in the uppermost Miocene deposits of southern Iloilo (Fig. 1). The *Globigerina nepenthes* population does not range as high in the section as does *Sphaeroidinella seminulina, Globoquadrina altispira globosa,* and others. Saito (*7*) reports *G. nepenthes* no higher than the Tortonian of Europe; however, I believe that it may range into the Sarmatian in a time sense (*3*, *8*). A stratigraphic section some 1500 m thick represents the post-*Globigerina nepenthes* strata in Iloilo (*3*); thus, a major unconformity is indicated for the boundary zone in the deep-sea cores of the rises, a hiatus representing some 10 to 12 million years of Pliocene time.

A third aspect of deep-sea cores is the question as to how unusual it is to find Tertiary strata exposed at the surface of the deep-sea floor. Tertiary faunas are exposed, or underlie a veneer of Pleistocene, on rises on the sea floor in many instances (*9*), so it is not unusual that later Miocene sediments underlie a veneer of Pleistocene sediments on the rises of the Atlantic and Indian oceans. Unconformities of this type are very difficult to recognize on the basis of lithologic evidence alone because of the similarity of globigerinid ooze above and below the contacts. Why the Pliocene is absent on so many rises on the deep-sea floor is a question yet to be answered; however, as suggested by Ericson *et al.* (*1*), the mechanism operating to eliminate part of the Pleistocene may be invoked to explain the absence of most or all of the Pliocene and parts of the Miocene. Tectonically, it would seem that submarine rises with a Miocene-Pleistocene contact may have developed during the Pliocene. Tectonic activity might have provided the triggering mechanism for some slumping; the development of a submarine rise would of itself remove the area from the category of an ideal depositional site. Submarine currents, internal waves, or some related phenomena prevented continuous sediment accumulation in the same manner as with truncated sea mounts (*6*, *10*).

A fourth aspect of the Miocene-

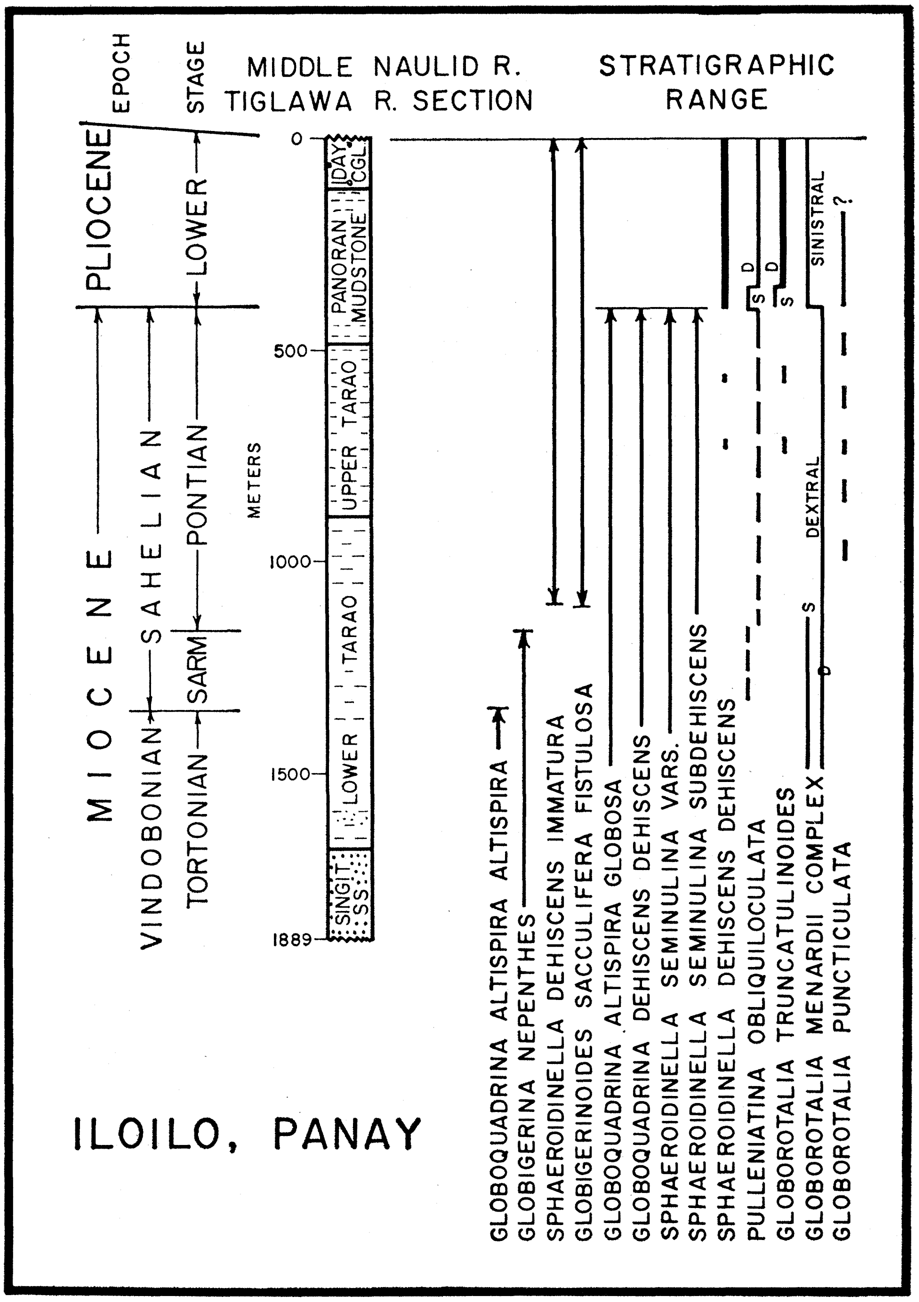

Fig. 1. Stratigraphic ranges of diagnostic planktonic foraminifera from a section measured along the Middle Naulid River and Tiglawa River, southern Iloilo, Panay, by the staff of Mr. William R. Merrill, Catawba International, Inc. These data are from my work on Philippine stratigraphy (*3*). *S* refers to sinistral or left-coiling; *D* refers to dextral or right-coiling.

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*).

ORVILLE L. BANDY
University of Southern California,
Los Angeles

References and Notes

1. D. B. Ericson, M. Ewing, G. Wollin, *Science* **139**, 727 (1963).
2. W. R. Riedel, M. N. Bramlette, F. L. Parker, *ibid.* **140**, 1238 (1963).
3. O. L. Bandy, *Bull. Am. Assoc. Petrol. Geologists*, in press.
4. A. G. I. P. Mineraria, *Foraminiferi Padani* (Donato, Milan, Italy, 1957).
5. P. J. Bermúdez, *Memoria dell III Congreso Geológico Venezolano, Tomo III Bol. Geología, publ. espec.* **3**, 1119-1393 (1961).
6. O. L. Bandy, *Science* **140**, 1402 (1963).
7. T. Saito, *Trans. Proc. Palaeont. Soc. Japan,* n. s. **48**, 331 (1962).
8. O. L. Bandy, *Micropaleontology*, in press.
9. F. B. Phleger, F. L. Parker, J. F. Peirson, *Repts. Swedish Deep-Sea Exped.* **7**, 1–122 (1953); C. Emiliani, *Science* **199**, 853 (1954); *J. Geol.* **63**, 552 (1955); *ibid.* **64**, 284 (1956).
10. E. L. Hamilton, *Geol. Soc. Am. Mem.* **64**, 1–97 (1956).
11. Contribution of the Allan Hancock Foundation, University of Southern California. I thank Richard K. Stouffer for drawing the figure and Maynard T. Smith for editing and typing assistance. I became interested in this problem as an outgrowth of current studies of deep-sea foraminifera which is a part of the U.S. Antarctic deep basin and trench research program for biological oceanology, supported by the National Science Foundation. As acknowledged in my work on planktonics of the Philippines (*3*), to which extensive references are made herein, I thank the following for permission to publish results of that Philippine study: W. R. Merrill and staff, Catawba International, Inc.; T. S. M. Tanneft and staff of San José Oil Co., Inc.; John T. Sinclair, Jr. and staff of the Catawba Corp.; James L. Buckley, president of San José Oil Co., Inc.; and the Philippine Oil and Development Co., Inc.

10 September 1963

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.