CaO, 1.83; Na_2O, 1.01; K_2O, 0.12; P_2O_5, 0.23; H_2O^+, 0.00; H_2O^-, 0.05; C, 0.05; FeS, 5.71; Fe, 6.46; Ni, 1.17; and Co, 0.06.

The history of this meteorite exemplifies the problems of effective recovery. Had the stone fallen a few meters farther east it would have landed in a vacant lot; even if it had been noticed by a casual passerby, probably the inconspicuous black stone would not have been retrieved for scientific study. By fortunate chance it landed on the warehouse roof with sufficient force to punch a hole and cause a leak. Such occurrences are naturally extremely rare: in 1958 LaPaz (*4*) recorded 27 meteorites (from Barbotan, France, in 1790 to Sylacauga, Alabama, in 1954) known to have damaged buildings.

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References and Notes

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5. We thank U.S. Plywood–Champion Papers Corp., parent company of Nationwide Papers, Inc., for presenting this meteorite to the U.S. National Museum, and for the cooperation and help of its staff.

10 April 1968

Oxygen-Isotope Ratios in Phosphate from Fossil Marine Organisms

Abstract. *Well-preserved fossil marine organisms generally yield very positive* $\delta^{18}(PO_4^{3-})$ *values which are considered to result from relatively good preservation of the original oxygen-isotope composition of phosphatic material deposited under isotopic equilibrium conditions in oceanic water whose* $O^{18}:O^{16}$ *ratio was more positive than that of modern oceans.*

Measurements of oxygen-isotope compositions of phosphate and carbonate from shells and skeletons of living and fossil marine organisms have been reported (*1*, *2*); a tentative equation for the phosphate-water isotopic temperature scale was given, together with the first group of measurements made on some Paleozoic and Mesozoic fossils. Several Jurassic and Cretaceous belemnites showed $\delta O^{18}(PO_4^{3-})$ values (*3*) so positive as to correspond to temperatures even lower than 0°C on the tentative scale established. This fact was considered to result from deposition of phosphatic material under isotopic equilibrium conditions in an oceanic water whose $O^{18}:O^{16}$ ratio was more positive than that of modern oceans.

We now report further measurements made on shells and skeletons of fossil marine organisms of Mesozoic and Tertiary ages. The fossils came mainly from North America and Europe (France, England, Germany, Belgium, Netherlands, Italy, Scotland, Denmark, Sweden, and the U.S.S.R.). Belemnites and pelecypods were mainly used, along with some fish teeth, brachiopods, and a few other organisms.

The technique used for purification of the phosphate of the samples, quantitative extraction of the oxygen by fluorination with bromine trifluoride, and its conversion to CO_2 for spectrometric measurements has been described (*1*). The standard deviation of the measurements is ± 0.2 per mille.

We have checked in some living pelecypods, belonging to the same (or similar) genera as some of our fossil specimens, that the phosphate contained in their shells is precipitated under isotopic equilibrium conditions. With regard to fish teeth, our measurements on living specimens confirm that, at least in the case of the species studied, the phosphate is precipitated under equilibrium (or quasi-equilibrium) conditions.

Our samples and results are listed in Table 1; results for samples 1 to 41 have been published (*2*). The $\delta O^{18}(PO_4^{3-})$ values are given versus the SMOW isotopic standard (*3*); they are plotted in Fig. 1 against the geological ages attributed to the fossils.

If one tries to interpret the results in Fig. 1 in terms of paleotemperatures, the temperature results are unreliable. From the most positive isotopic data, and assuming that δ-water is zero, we calculate temperatures that are generally not far from 0°C. On the other hand one cannot calculate both the temperature and the oxygen-isotope composition of ocean water from a phosphate-carbonate isotopic temperature scale (*2*).

We assume that the wide range of isotopic values obtained for each geological level is due only to effects of postdepositional isotopic exchange between the fossils and groundwater. This assumption is confirmed by an evident positive relation between the isotopic values and the degrees of preservation of the fossils. Other evidence of postdepositional exchange processes is the fact that Paleozoic fossils always show very negative and very uniform values in their phosphate-isotope composition. A freshwater fossil (*Antraconauta phillipsii*, sample 32) shows (*2*) the same oxygen-isotope composition as do the sea-water fossils *Obolus* and *Lingula* whose $\delta O^{18}(PO_4^{3-})$ values are close to the δO^{18} value that can be calculated for a phosphate in isotopic equilibrium with rainwater at room temperature.

The isotopic values from belemnites are generally more positive than those from coeval pelecypods or brachiopods as to both carbonate and phosphate. This fact seems quite reasonable if one assumes that (i) isotopic exchange processes for phosphate and carbonate were similar, the only difference being a different rate of exchange; and (ii) the shape of belemnites (very compact structure and relatively small exchange surface) is the best suited for slowing postdepositional exchange processes. The possibility that exchange processes occur normally between fossil shells and groundwater, even rapidly (geologically speaking), is indicated indirectly by the work of Fanale and Schaeffer (*4*); determination of the ages of fossil shells, by the helium-uranium method, led to the conclusion that in the case of Eocene, Oligocene, and Miocene fossils there was evident exchange of uranium between the fossil and local groundwater. It seems quite reasonable that similar exchange processes occur normally in the case of oxygen isotopes. Carbonates should exchange at a much higher rate than do phosphates because of the difference in the activation energies, and the difference in the energy bond between oxygen and C or P atoms.

Let us assume that only the fossils that show very positive $\delta O^{18}(PO_4^{3-})$ values have preserved reasonably well the original isotopic compositions. Starting from such a consideration it seems obvious that we should try to explain our results by assuming that the phosphate of the fossil shells and skeletons was precipitated under isotopic-equilibrium conditions, at unknown temperatures, in oceanic water whose oxygen-isotope composition was more positive than that of modern ocean water.

The oxygen-isotope composition of

ocean water should have changed between the Lower Jurassic and the Eocene, following qualitatively the path described by the dotted line in Fig. 1. This curve is purely indicative because it follows roughly the variation given by the most positive δO^{18}-(PO_4^{3-}) and does not take into account the possibility of superimposition of, for example, temperature effects.

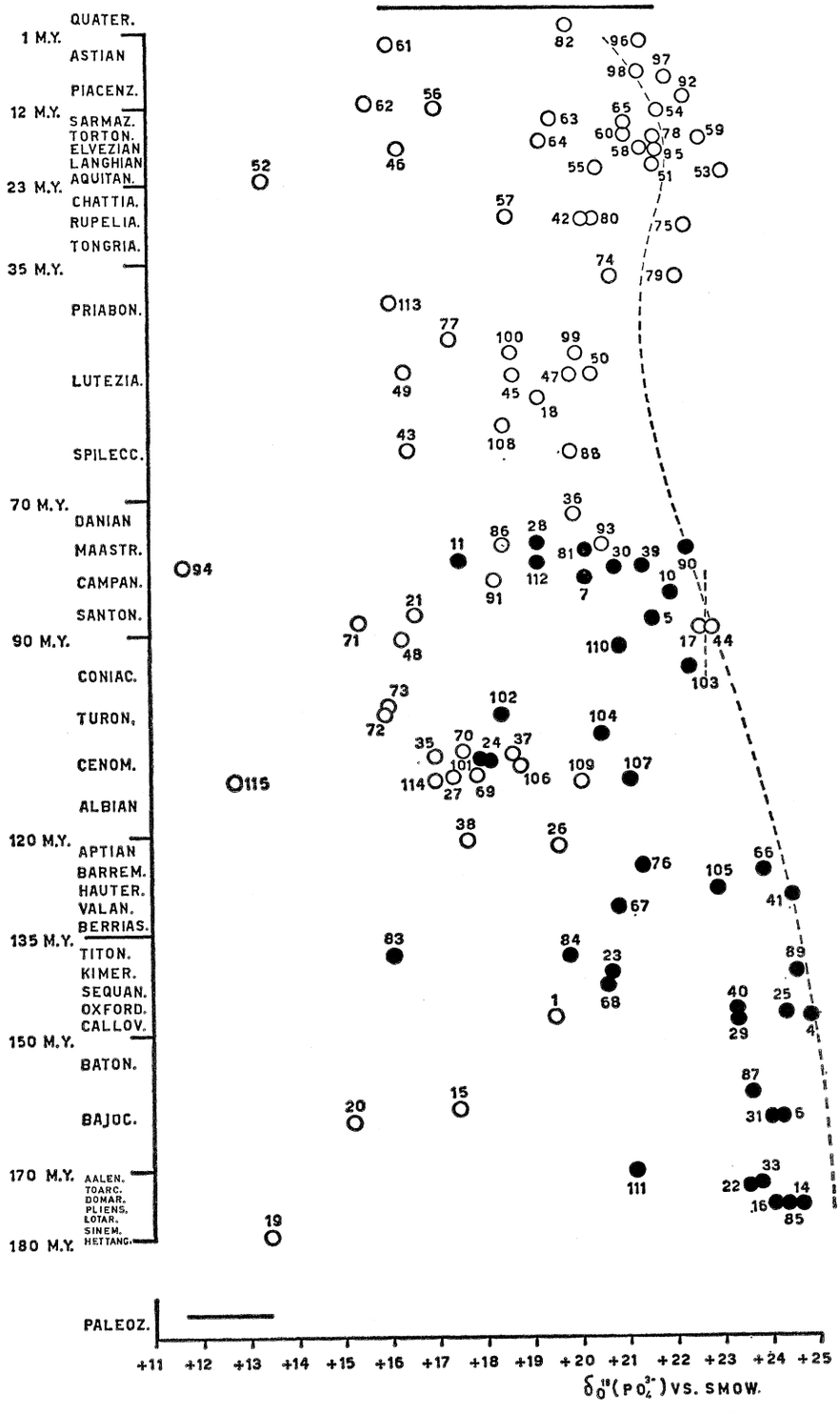

Fig. 1. Oxygen-isotope compositions of phosphate, versus the SMOW standard, plotted against geological ages for fossil shells and skeletons of marine organisms. Numbers refer to Table 1 and to published results (*2*). The horizontal lines at bottom and top represent the ranges of values yielded by Paleozoic fossils and living marine organisms, respectively. In the case of living organisms, the $\delta O^{18}(PO_4^{3-})$ are corrected for the isotopic effect of the environmental water. Solid circles, belemnites; open circles, other fossils. The dotted curve from Lower Jurassic to upper Tertiary represents qualitatively the proposed variation in the oxygen-isotope composition of ocean water through geologic time.

The very positive oxygen-isotope composition of ocean water, and post-depositional exchange processes, should have masked possible climatic variations which, however, should be very difficult to detect even if one measured many specimens from coeval sediments at different latitudes. In fact the isotopic compositions of specimens from different parts of the world are probably influenced by not only the climatic conditions during the life of the organisms but also different conditions during diagenesis of the sediments.

Regarding the lack of positive results from the Middle Cretaceous we must point out that none of our fossils from Albian and Cenomanian formations were really well preserved. Our results from Tertiary fossils need discussion from a different point of view. Beginning with the Upper Eocene, our most positive results shift in the direction opposite from that followed by the Mesozoic samples. Only during the Pliocene does there seem to be a tendency toward more negative results. The first possible interpretation of such behavior is that it may represent the effect of progressive climatic deterioration that may have resulted from either polar wandering or increasing continentality and orogenesis. Both paleontological and paleobotanical evidence prove that the climate varied during the Tertiary. One cannot indicate within an order of magnitude in degrees Celsius the decrease in average temperature, but there is no doubt that very low temperatures were not reached at middle latitudes. On the contrary, the most positive data from Miocene samples are not far from the isotopic values to be expected for temperatures around 0°C if one assumes an isotopic composition of water equal to the mean of modern ocean water.

Our interpretation of these results is based on the following considerations: there is geologic evidence of deposition of large evaporite formations during the Tertiary (*5*). From Eocene evaporites of North Africa, through Oligocene formations in the Rhine graben (Germany) and the Ebro basin (Spain), we go to the Lower Miocene evaporite belt that one can trace through Syria, Iraq, and Iran (where the evaporite sediments attain more than 1000 m in thickness) into Gujarat on the west coast of India. Vast deposits

of Lower, Middle, and Upper Miocene ages are common in Europe; sometimes Pliocene deposits also are present. It is established that the conditions for deposition of these large evaporite formations were not determined by climatic evolution toward a warmer climate, but only by the presence of a great arid belt similar to the one existing today at low latitudes in North Africa and at higher latitudes in Asia. This belt shifted with time northward or southward probably according to wandering of the poles.

Very likely the evaporation of large water masses during the Upper Eocene, Oligocene, and Miocene determined large variations in the oxygen-isotope composition of the water in relatively small basins like the Mediterranean, and in the surface waters and littoral areas of larger basins. If we admit the possibility of ice caps in the polar areas during the Oligocene and Miocene, such evaporation, occurring for about 2×10^7 years, may have slightly influenced also the isotopic composition of oceanic basins. According to the theory of continental drift, the Atlantic during the Middle Tertiary was narrower than it is today. This point could account for maximum variation of the oxygen-isotope composition of sea water in basins like the Mediterranean, a smaller effect in the water of the Atlantic, and a minimum effect (or none at all) in the Pacific. When we consider that the isotopic composition of modern Mediterranean water is from 1 to 1.5 per mille more positive than that of mean ocean water, a δO^{18} of 2.0 to 3.0 per mille for Miocene Mediterranean water does not seem exaggerated. In the case of surface water of the modern Atlantic, measurements of the oxygen-isotope composition range between 0.3 and 1.3 per mille (*6*), high latitudes excepted. A δO^{18} value of about 1 to 2 per mille seems reasonable for Miocene Atlantic surface water at middle and low latitudes. These assumptions, together with a limited deterioration of climate, could explain qualitatively or semiquantitatively our results from Tertiary fossils.

The data from upper Tertiary fossils were confirmed by measurement of the oxygen-isotope composition of inorganic phosphate (phosphate marine nodules) from various sources; the results will be published (*7*). Measurements from Miocene and Pliocene phosphate nodules yielded values very similar to those from fossils of the same

Table 1. Oxygen-isotope compositions of phosphate and carbonate from fossil shells and skeletons of marine organisms. Abbreviations (age): M., Middle; L., Lower; U., Upper.

Sample			δO^{18}-(PO_4^{3-}) vs. SMOW	δO^{18}-(CO_3^{2-}) vs. PDB-1
No.	Species	Age, source		
42	*Lamna cuspidata*	M. Oligocene, Germany	+ 20.2	
43	*Lamna* sp.	L. Eocene, France	+ 16.4	
44	*Pseudoranenella* sp.	Turon-Maastricht., Greenland	+ 22.8	
45	*Ostrea stewarti*	Eocene, Calif.	+ 18.7	− 5.8
46	*Ostrea titan*	M. Miocene, Calif.	+ 16.3	− 4.8
47	*Ostrea crenulimarginata*	M. Eocene, Ala.	+ 19.9	− 3.0
48	Unknown (fish vertebra)	Coniac.-Santon., Kans.	+ 16.3	
49	*Cucullea gigantea*	Eocene, Va.	+ 16.3	− 2.6
50	*Ostrea* sp.	M. Eocene, Ala.	+ 20.4	− 1.0
51	*Ostrea thomasii*	L. Miocene, Md.	+ 21.7	+ 0.1
52	*Discinisca* sp.	U. Olig.—L. Mioc., Calif.	+ 13.4	
53	*Ostrea percrassa*	L. Miocene, Md.	+ 23.2	+ 0.5
54	*Lopha sculpturata*	Miocene-Pliocene, Va.	+ 21.8	+ 0.7
55	Unknown (shark tooth)	L. Miocene, Calif.	+ 20.5	
56	*Crassostrea* sp.	Neogene, Israel	+ 17.1	− 8.0
57	*Cubitostrea compressirostra*	U. Paleocene, S.D.	+ 18.6	− 2.1
58	*Ostrea* sp.	Miocene, Md.	+ 21.4	− 1.4
59	*Discinisca lugubris*	Miocene, Va.	+ 22.7	− 4.8
60	*Discinisca* sp.	Miocene, Calif.	+ 21.1	
61	*Ostrea vespertina*	U. Pliocene, Calif.	+ 16.1	+ 0.4
62	*Ostrea herrmanni*	U. Mioc.–L. Plioc., Calif.	+ 15.6	− 8.0
63	*Ostrea titan*	U. Miocene, Calif.	+ 19.6	+ 0.1
64	*Ostrea* sp.	Miocene, Calif.	+ 19.3	+ 0.5
65	*Isurus* sp. (tooth)	Miocene, Calif.	+ 21.1	
66	*Oxyteuthis cfr. jasikowi*	Barremian, Canada	+ 23.9	+ 0.5
67	*Acroteuthis impressa*	Valanginian, Canada	+ 20.8	− 5.2
68	*Belemnites* sp.	U. Jurassic, Wyo.	+ 20.5	+ 0.7
69	*Exogyra columba*	Cenomanian, Israel	+ 17.9	− 2.8
70	*Exogyra flabellata*	Cenomanian, Israel	+ 17.6	− 3.7
71	*Crassostrea soleniscus*	Cenom.–U. Creta., Tex.	+ 15.4	− 6.1
72	Unknown (ray tooth)	Turonian, S.D.	+ 15.9	
73	Unknown (shark tooth)	Turonian, S.D.	+ 16.0	
74	*Gryphaea gigantica*	U. Priabonian, Italy	+ 20.8	− 2.1
75	*Ostrea* sp.	M. Oligocene, Italy	+ 22.4	− 0.8
76	*Acroteuthis impressa*	Barremian, Canada	+ 21.3	− 5.3
77	*Ostrea bersonensis*	L. Priabonian, Italy	+ 17.3	− 2.6
78	*Ostrea* sp.	M. Miocene, Italy	+ 21.7	− 3.5
79	*Pycnodonta brongnarti*	U. Priabonian, Italy	+ 22.2	− 0.9
80	*Lamna cuspidata*	M. Oligocene, Germany	+ 20.4	
81	*Belemnitella americana*	Maastrichtian, N.J.	+ 20.2	− 0.0
82	*Disciniscus cumingii*	U. Quatern., Baja Calif.	+ 19.9	− 1.9
83	*Hibolites arkelli*	L. Titonian, New Zealand	+ 16.1	− 0.9
84	*Hibolites m. marwicki*	L. Titonian, New Zealand	+ 19.8	− 2.2
85	*Passaloteuthis* sp.	Pliensbachian, Germany	+ 24.4	− 1.4
86	*Biradiolites aquitanicus*	Maastrichtian, France	+ 18.4	− 4.2
87	*Belemnites* sp.	U. Bajocian, Greenland	+ 23.6	− 1.5
88	*Lamna* sp.	L. Eocene, Italy	+ 19.9	
89	*Belemnites* sp.	U. Kimeridgian, Greenland	+ 24.6	− 1.0
90	*Belemnitella americana*	Maastrichtian, N.J.	+ 22.3	+ 0.2
91	*Lamna* sp.	Campanian, Belgium	+ 18.2	
92	*Oxyrhina spallanzanii*	L. Pliocene, Italy	+ 22.4	
93	*Pycnodonta vesicularis*	Maastrichtian, Ala.	+ 20.5	− 1.9
94	*Unio* sp.	U. Creta., Ariz.	+ 11.7	− 11.7
95	*Pycnodonta* sp.	L. Miocene, Italy	+ 21.8	+ 0.4
96	*Lopha* sp.	U. Pliocene, Fla.	+ 21.5	− 0.4
97	*Lopha* sp.	Pliocene, N.C.	+ 22.0	+ 0.7
98	*Pycnodonta* sp.	Pliocene, Italy	+ 21.4	+ 0.4
99	Unknown (fish tooth)	Eocene, Ala.	+ 20.1	
100	Unknown (fish tooth)	Eocene, Ala.	+ 18.7	
101	*Belemnites* sp.	Cenomanian, Belgium	+ 18.0	− 0.6
102	*Actinocamax plenus*	Turonian, Belgium	+ 18.4	+ 0.4
103	*Actinocamax subventricosus*	Coniacian, Sweden	+ 22.4	− 0.2
104	*Actinocamax* sp.	L. Turonian, Belgium	+ 20.5	− 0.5
105	*Belemnites* sp.	Neocomian, Madagascar	+ 22.9	+ 0.4
106	*Oxyrhina mantelli*	Cenomanian, England	+ 18.8	
107	*Neohibolites minimus*	Alb.-Cenom., England	+ 21.1	− 0.6
108	*Lamna obliqua*	L. Eocene, England	+ 18.5	
109	*Lamna* sp.	Alb.-Cenom., England	+ 20.1	
110	*Belemnitella* sp.	L. Senonian, England	+ 20.9	− 1.5
111	*Acrocoelites triscissus*	Aalenian, France	+ 21.2	− 1.9
112	*Belemnitella mucronata*	U. Senonian, England	+ 19.2	− 0.2
113	*Lamna elegans*	U. Eocene, England	+ 16.1	
114	*Lamna* sp.	Alb.-Cenom., England	+ 17.0	
115	*Isurus* sp.	Alb.-Cenom., England	+ 12.8	
116	Unknown (shark tooth)	Pliocene, Italy	+ 19.7	

ages. It seems improbable that completely different materials (shells and inorganic phosphate nodules) should show the same very positive isotopic compositions by chance or as a result of unknown postdepositional processes. Thus we may reasonably consider the most positive data from Miocene fossils to result from good preservation of the original isotopic composition of the phosphate precipitated in isotopically positive waters.

The hypothesis proposed to interpret the results from Mesozoic and Tertiary fossils seems rather difficult to accept because it changes widely our ideas of the isotopic history of the oceans and of the rate of the isotopic-exchange processes affecting fossils throughout geologic time. The supposed variation of the oxygen-isotope composition of ocean water [about 5 to 7 per mille (*8*) during about 2×10^8 years] is very great but does not seem unbelievable (*2*). The sedimentation (either chemical or biologic) of carbonate, phosphate, sulfate, silicate, and such materials may be considered responsible for such variation, because of the enrichment in oxygen-18 of the different chemical compounds relative to ocean water. We must admit that acceptance may be difficult of the hypothesis proposed to explain our $\delta O^{18}(PO_4^{3-})$ results, but we assume that there are no serious arguments for rejection.

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8. These values can be approximately evaluated if one assumes an average temperature of 15° to 20°C for the Jurassic ocean and calculates the δ-difference on the basis of the most positive $\delta O^{18}(PO_4^{3-})$ obtained from Jurassic belemnites.
9. Supported by C.N.R.–C.N.E.N. contract 115-1159-1472 and by NSF grant GA-351. We thank G. Giaconi and P. Perusini for assistance.

13 March 1968

Photolytic Cleavage of Sulfonamide Bonds

Abstract. *It has been found that the sulfonamide bond is relatively susceptible to photolytic cleavage. The breakdown was effected either by irradiation with a source having a continuous emission above the wavelengths of 1800 angstroms or by another source emitting principally at 2537 angstroms. Less destruction of the amino acids was seen with the latter relative to the sulfonamide bond cleavage. The cleavage was not effected by irradiation at wavelengths greater than about 3000 angstroms. Side reactions were noted involving decarboxylation, demination, and destruction of certain susceptible amino acids such as tryptophan. In only one case was a product found that arose from cleavage of a carboxamide bond; glycyltyrosine gave glycine and tyrosine upon irradiation. A yield of 75 percent of the corresponding amino acid has been obtained by irradiation of tosylhistidine; yields of 75 to 100 percent have been obtained from sulfamic acid (NH_2SO_3H). A qualitative method for identifying sulfonylated amino acids is described.*

We report here some observations on the effect of ultraviolet light on compounds containing the partial structure —SO_2NH—. We have found that the sulfonamide bond is susceptible to photolytic attack under conditions where many other bonds in organic molecules are attacked to a minor degree (*1*). In particular, the photolytic S—N bond cleavage in the sulfonylated amino acid and peptide derivatives is the change most in evidence for all of the amino acid derivatives examined except for the derivatives of cystine, cysteine, and tryptophan. Although the yields of the released amino acid are not yet high enough to make the process a serious contender for deblocking, say, tosylated amino acids, we do not feel that the highest yields have yet been attained. Aside from the potential use in the area of peptide synthesis, the cleavage is intrinsically interesting because of the relative ease with which this cleavage may be effected.

Historically the removal of a tosyl group (*p*-toluenesulfonyl-) from tosylated amino acids and peptides can be achieved without appreciable cleavage of the peptide bonds by treatment of these derivatives with hydrogen iodide (*2*). Cleavage of sulfonamide bonds by anhydrous hydrogen bromide (*3*) has been extended successfully to peptide derivatives (*4*). Treatment with sodium in liquid ammonia provided a generally applicable deblocking procedure (*5*). The photolysis of the appropriate amino acid and peptide derivatives may be a potential new method of removing a blocking group commonly used in peptide synthesis.

The ultraviolet energy sources used were a Hanovia utility quartz lamp (Hanovia) and a germicidal lamp (General Electric, 25 watt, G25T8). The former has a continuous spectrum from 1800 Å through the visible; the latter gives a sharp line at 2537 Å and relatively little else except in the visible. Some of the quantitative determinations of the free amino acids formed from the derivatives are shown in Table 1. Solutions of tosyl amino acids (1 ml in volume) were kept under mineral oil during exposure to ultraviolet. The exposures were carried out in transparent quartz test tubes (1.5 by 10 cm) (Fig. 1) situated at a distance of 1.5 cm from the Hanovia lamp. The temperature of the solution was maintained at the desired level by using a "cold finger" probe (Fig. 1). The optimum time was used in obtaining the yields shown in Table 1, since the released amino acid

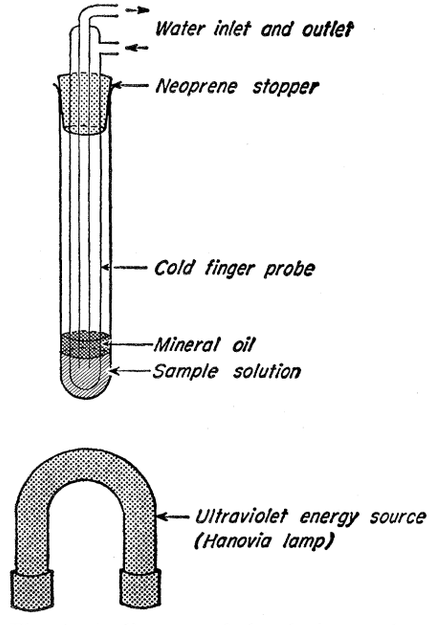

Fig. 1. A diagram of the device used to provide a controlled temperature during irradiation with the Hanovia lamp. Water, or a glycerol-water mixture, was pumped through the "cold finger" probe from a constant temperature bath.