

are multiples of m . The noise power, the sum of the coefficients in the noise power spectrum, is thus reduced by a factor of m ; and the average noise amplitude, the square root of the noise power, is reduced by a factor of $m^{1/2}$.

The effect of R_m on the signal power cannot be determined without a detailed knowledge of the spectrum of the signal. If the signal contains only elements of m -fold symmetry then all signal components are of frequencies harmonic to m and the signal, hence the signal power, is left unchanged; the signal-to-noise power ratio is increased by a factor of m . If the signal contains components at other frequencies, they will be eliminated and the signal power will be decreased, resulting in an improvement in signal-to-noise ratio by a factor less than m . Alternatively, if the noise is not white, the noise power will be reduced, in general, by a factor less than m , and again the improvement in signal-to-noise ratio will be less than m .

The rotation technique, therefore, is not completely equivalent to the signal-averaging technique used in electrophysiology because of the possible presence of signal frequencies not harmonic to the order of rotation, anomalous reinforcements and a loss in noise reduction resulting.

The presence of heavy noise in the original data will tend to produce reinforcements for all rotation orders, because the noise does contain components of all orders of symmetry. However the number of lobes in the patterns produced by noise will be equal to the rotation order, and application of the rules previously described produces the fundamental degree of symmetry $x = 1$.

A convenient mechanism for performing the rotation operation can be constructed along the lines suggested by the stroboscopic method of Markham *et al.* (1). The photograph (or transparency) is held stationary and (trans) illuminated with a stroboscopic light source. The image is rotated optically, a dove prism (5) driven by an electric motor being used. The stroboscope may be triggered by a photoelectric commutator attached to the rotating prism. This method provides the convenience of having a stationary photograph, for easy centering and adjusting, as well as having the advantage of immediate viewing of the image.

RICHARD S. NORMAN
Program in Communication Sciences,
University of Michigan, Ann Arbor

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3. Proof: $L = mx/(m,x)$, where (m,x) is the greatest common divisor of m and x . Hence $x = L/k$, where $k = m/(m,x)$ is a divisor of m and $(k,L/m) = [m/(m,x), x/(m,x)] = (m,x)/(m,x) = 1$.
4. The coefficient of any frequency in the power spectrum is the square of the absolute value of the corresponding coefficient of the regular Fourier expansion.
5. Available from Edmund Scientific Co., 101 East Gloucester Pike, Barrington, New Jersey 08007. Note that the dove prism doubles the angle of revolution; one revolution of the prism rotates the image by two revolutions.
6. Support provided by a NSF predoctoral fellowship.

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Potassium-Argon Geochronology of Deep-Sea Sediments

Abstract. A potassium-argon dating method applicable to small quantities of volcanic minerals and glass has been developed and used to determine the ages of North Pacific sediments. Tertiary sedimentation rates range from less than 1.0 millimeter per 10³ years for deep-sea "red clay" to 1 centimeter per 10³ years for calcareous-siliceous ooze nearer the continent. The potassium-argon ages obtained from different minerals are concordant, and in samples with associated fossils, these ages are compatible with the paleontologic evidence.

Our present understanding of the time relationships of pelagic sediments is based upon radiometric methods which apply only to the past 500,000

years (1) and upon paleontologic studies. If we are to extend our knowledge of open-ocean sediments to the more remote past and to the vast non-fossiliferous areas of the oceans, we shall require new dating techniques. The use of potassium-argon analysis of volcanic debris to date pelagic sediments has been suggested (2) as a means of reconciling discrepancies between existing dating techniques. This suggestion led to the development of a K-Ar technique, which is applicable to small quantities of volcanic contributions found in pelagic sediment cores, and has permitted the assignment of ages to several cores from the Pacific.

The usual assumptions of K-Ar dating (a closed system and no argon present at time zero) must be amplified if the age obtained from volcanic materials is to correspond to the time of deposition as follows: (i) The volcanic material must arrive at the depositional site soon after its formation during the volcanic episode. (ii) Continental detritus, submarine erosional products, or authigenic marine minerals must not be present in the analyzed material. By choosing samples from volcanic ash layers, detrital contamination is minimized, and one can be relatively sure of dealing with a short-term volcanic event. The low temperatures of the marine abyssal environment (approximately 1°C) greatly reduce the possibility of argon loss by diffusion.

Cores containing obvious volcanic contributions, either in the form of altered ash beds or concentrations of fresh volcanic glass, were chosen for

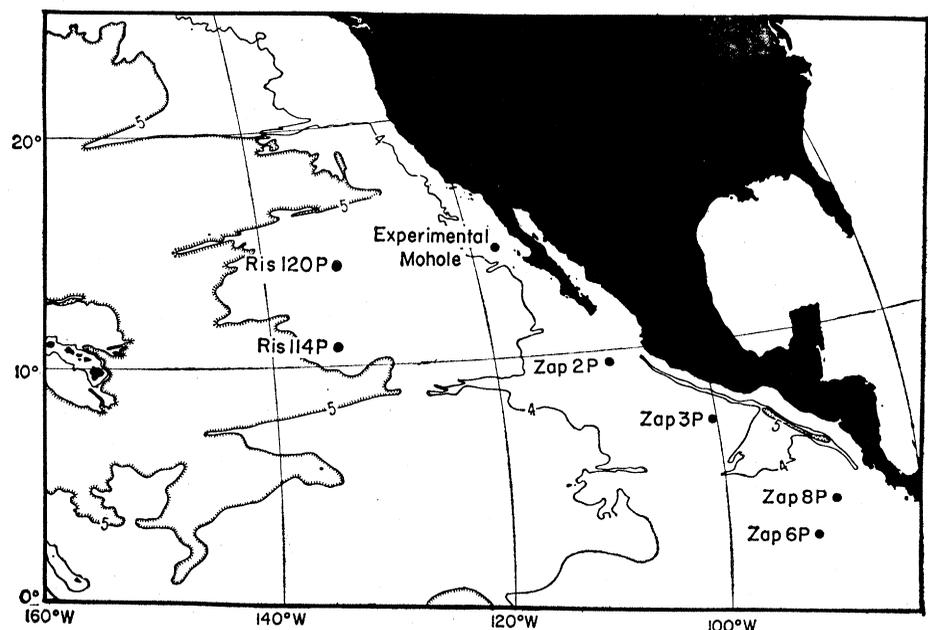


Fig. 1. Location of cores. Contours in thousands of meters.

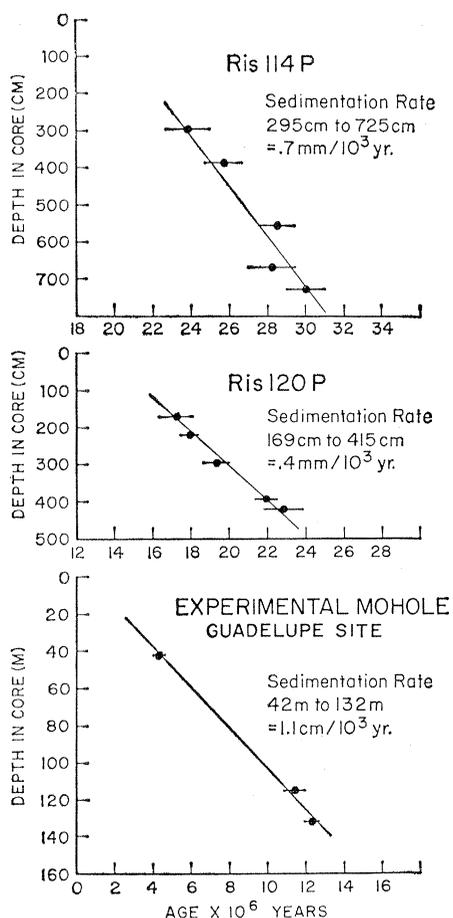


Fig. 2. Plot of age versus depth in the core.

Table 1. Potassium-argon data from seven deep-sea cores. Constants used in age calculations: $\lambda_{\beta} = 4.72 \times 10^{-10} \text{ year}^{-1}$, $\lambda_{\alpha} = 0.584 \times 10^{-10} \text{ year}^{-1}$, $K^{40}/K = 0.000119$.

Sample depth (cm)	Material dated	K (%)	Ar ⁴⁰ radiogenic (%)	Age (10 ⁶ years)
<i>Ris 114P, 21°33'N 134°W, 5040 m</i>				
295	Anorthoclase	3.58	38	23.8 ± 1.2
385	Anorthoclase	3.27	51	25.7 ± 1.0*
554	Anorthoclase	2.68	42	28.3 ± 1.0*
554	Biotite and amphibole	3.66	46	28.9 ± 1.5
667	Sanidine	5.60	70	28.2 ± 1.4
725	Anorthoclase	2.90	65	30.8 ± 1.1*
725	Biotite and amphibole	5.45	20	28.2 ± 1.5
<i>Ris 120P, 28°19'N 133°12'W, 4420 m</i>				
169	Plagioclase	1.86	47	17.2 ± 0.9
218	Plagioclase	0.78	20	17.5 ± 0.6*
218	Sanidine	8.13	64	18.2 ± 0.7
295	Plagioclase	0.86	23	19.3 ± 0.7*
392	Plagioclase	0.96	25	21.9 ± 0.6*
416	Anorthoclase	3.56	48	22.8 ± 1.1
<i>Experimental Mohole, 28°59'N 117°30'W, 3566 m</i>				
46, No. 9-1	Glass	3.34	16	4.3 ± 0.3
133, No. 8-13	Glass	4.26	46	11.4 ± 0.6
89, No. 8-15	Glass	4.13	42	12.3 ± 0.4*
<i>Zap 2P, 17°59'N 109°31'W, 3640 m</i>				
190	Glass	3.95	25	0.65 ± 0.05
<i>Zap 3P, 14°14'N 100°32'W, 3450 m</i>				
257	Glass	3.40	15.5	0.49 ± 0.04*
<i>Zap 6P, 5°23'N 91°45'W, 3700 m</i>				
172	Glass	3.32	8.2	0.50 ± 0.04*
355	Glass	3.44	6.5	0.98 ± 0.10
<i>Zap 8P, 7°46'N 88°46'W, 3500 m</i>				
171	Glass	3.35	9.3	0.53 ± 0.04*

* Indicates the average of two analyses.

study. From these pyroclastic sediments, minerals or glasses demonstrated by previous workers to be argon-retentive were separated for K-Ar analysis. As a result of the restricted amount of material available from deep-sea cores, the final weight of datable material coarser than 37μ was generally only a few tens of milligrams. Samples of this size require refined techniques for both potassium and argon analysis. Potassium was analyzed either by flame photometry with lithium internal standard and sodium buffer (3) or by atomic absorption with sodium buffer. A high-sensitivity omegatron mass spectrometer (4) proved ideal for the analysis of the argon in these small samples.

Of the cores analyzed (Fig. 1 and Table 1), Ris 114P and Ris 120P are similar and will be discussed together. Both are from the "red clay" area of the North Pacific and contain no calcium carbonate or opal. Samples were selected from what I interpret as locally derived volcanic ash layers in which the volcanic glass has been altered to phillipsite. Each volcanic event is recorded in the core as a lighter colored band of nearly pure phillipsite; however, this band does contain concentrations of unaltered feldspar, biotite, and am-

phibole in the size fraction coarser than 37μ . Sufficient feldspar was present at all sampled levels to obtain a K-Ar age, and at three levels, Ris 114P (554 and 725 cm) and Ris 120P (218 cm) ages were obtained from coexisting minerals. The ages of coexisting minerals agree within the limits of error, which strongly suggests that the assumptions of the method are being met. It is unlikely that any violation of the assumptions would have operated on different minerals in such a way that the same age would result.

Dates were not obtained above 295 cm in Ris 114P or above 169 cm in Ris 120P because volcanic layers are not present in the higher levels. Sedimentation rates determined from the dated part of the cores (Fig. 2) are lower than those reported for the North Pacific during the last 400,000 years by the ionium-thorium ($\text{Th}^{230}/\text{Th}^{232}$) method but are about the same as those reported in the South Pacific (5). Extrapolating the K-Ar rates to the core surface gives 14 million years for the surface sediment of Ris 120P and 20 million years for the surface sediment of Ris 114P. Quite likely the surface sediment is not this old, but rather a hiatus may exist in the upper part of the core. Such missing sections are common in Pacific pelagic cores, for reasons not fully understood (6). An alternative explanation is a drastically lower but steady accumulation of sediment in the upper part of the cores.

Three samples from the experimental Mohole drilling (Guadelupe Site) (Table 1) were chosen for analysis because (i) paleontologic studies of nannoplankton and Foraminifera have provided stratigraphic age indications and (ii) acidic volcanic glasses are abundant at a number of levels in the core. The paleontological age of sample 9-1, at 46 cm, should be near the Pliocene-Miocene boundary according to Martini and Bramlette (7). However, Bramlette (8) states that the rare and less diagnostic fossils present in this sample do not preclude a Pliocene age. It was positioned in the sequence mainly on the basis of indicated depth which may be in error since this was the only sample from the 9-1 drill hole. The 4.3-million-year age (Table 1) which I have determined for this sample is younger than the Pliocene-Miocene boundary age of 7 million years suggested by Funnell (9) on the basis of other K-Ar determinations. Martini and Bramlette (7) place the Tortonian-Helvetian boundary between sample 8-

13 at 133 cm and sample 8-15 at 89 cm. Previous K-Ar data (9) would suggest an age of about 15 million years for this part of the Miocene, which is somewhat older than the 11.4 and 12.3 million year ages which I have determined for samples 8-13 and 8-15, respectively. Considering the problems of correlating this core with previously dated stratigraphic sections on land, as well as the errors of the K-Ar measurements, this agreement is considered satisfactory. The sedimentation rate for this predominately calcareous-siliceous ooze between sample 9-1 at 46 cm and sample 8-15 at 89 cm (42 to 132 meters below the sediment surface) is 1.1 cm/10³ years. This compares with an ionium-thorium rate of 8 mm/10³ years, determined on a gravity core, 230 centimeters long, from the same area (5).

The use of acidic glasses to record time in marine sediments was extended to a series of four cores taken in the waters off Central America (Fig. 1). Cores from this area commonly contain layers of volcanic glass, many of which are remarkably pure bands of acidic glass shards, perhaps similar in origin and type to those described by Worzel (10). Here the assumptions of rapid deposition and exclusion of detritus are most probably fulfilled, and there is little reason to suspect an argon loss by diffusion during this time range (less than 10⁶ years). The rates of accumulation for these cores range from 3.0 mm/10³ years to 5.0 mm/10³ years. Cores Zap 3P, Zap 6P, and Zap 8P each contain an ash layer which gives an age that agrees within the limits of error, so that these layers may have originated from the same volcanic event.

N-Acetylhistidine Isolated from Frog Heart

Abstract. A diazo-positive compound was found in an extract of frog heart. This substance showed a negative ninhydrin reaction and had on a paper chromatogram developed with a phenol-hydrochloric acid solvent system a higher R_F than carnosine. The substance, isolated by chromatography, was identified as N-acetyl-L-histidine.

Carnosine is contained in heart tissue as well as the skeletal muscle of various vertebrates (1). Paper chromatograms, developed by 80 percent phenol in an atmosphere of HCl (2), of hot-water extracts of animal hearts, indicated the presence of two diazo-reacting substances, histidine and carnosine.

In frog heart tissue we discovered another unique diazo-positive compo-

In summary, this initial study indicates that K-Ar geochronology can be applied to the volcanic phases of pelagic sediments and that it is a means of dating the time of deposition. The long half-life makes it applicable to the entire Tertiary, and careful work may permit its application to materials less than 100,000 years in age. The limiting feature of the method is its reliance upon volcanic contributions. However, the abundance of submarine volcanoes, particularly in the Pacific (11), and the common occurrence of volcanic contributions in pelagic sediments (12) suggest that it has wide application.

JACK R. DYMOND

University of California, La Jolla

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(iii) a mixture of *n*-propanol and 1*N* acetic acid (3 : 1). This newly isolated substance was ninhydrin-negative.

After digestion for 2 hours in 6*N* HCl at 100°C, a ninhydrin- and diazo-positive spot corresponding to histidine was detected on the paper chromatograms, an indication of an *N*-substituted amino acid.

Paper electrophoresis with a barbiturate buffer (pH 8.6, 0.075*M*) or a pyridine-acetate buffer (pH 4.0, 0.1*M*) indicated that the substance was more acid than neutral amino acids.

The hydrolyzate was analyzed for acyl groups by a chromatographic technique (3), and the analysis indicated the presence of either an acetyl or a formyl group.

Acylylhistidines including succinyl-, propionyl-, acetyl- and formylhistidines were synthesized, and the substance was compared with these standards. In solvent systems of 80 percent phenol in an atmosphere of HCl; a mixture of *n*-butanol, acetic acid, and water; a mixture of *n*-propanol and 1*N* acetic acid; or others, the R_F values of the unknown component coincided well with that of acetylhistidine. However, in a developing mixture of lutidine and collidine the substance had a lower R_F value than acetylhistidine or formylhistidine. The substance mixed with authentic acetylhistidine yielded two different spots in this solvent system. Unequivocal identification of the unknown component was therefore not possible.

At this stage, large quantities of bullfrog (*Rana catesbeiana*) hearts became available and were stored in 95 percent ethanol. The substance was easily extracted from about 300 frog hearts with 1 liter of ethanol. The ethanol was evaporated and the residue was treated with ether, to remove fatty impurities. The residue was then dialyzed against distilled water for about 12 hours and the outside fluid was concentrated at reduced pressure.

The water-soluble residue was chromatographed (3.0- by 140-cm column) with a pyridine-acetate buffer (pH 3.1, 0.1*N*) on Dowex 50-x8 (300 to 400 mesh, buffered at pH 3.1). Each 10 ml of the effluent was collected mechanically; fractions that were diazo-positive and ninhydrin-negative were pooled and evaporated at reduced pressure. The product still contained a trace amount of ninhydrin-positive impurities that could not be removed by column chromatography on Dowex-1.

Preparative paper chromatography