17. RADIOMETRIC AGE DETERMINATIONS

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INTRODUCTION

Rock samples from Leg 26 sites were submitted to the Institute of Geological Sciences, London, and to Dalhousie University, Halifax, N. S., for radiometric age determination. The results of these determinations are presented in this short contribution. Because of the shortage of time resulting from a strict publication schedule, the results of the two studies are presented as two separate reports and no attempt has been made to combine them in a general closing discussion.

K-Ar AGE DETERMINATIONS ON SAMPLES OF DEEP-SEA BASALTS[1]

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Introduction and Sampling

Potassium-argon analytical data on a suite of oceanic basalts received from the Deep Sea Drilling Project are given in the accompanying table (Table 1). The first batch of samples was received in the form of finely powdered material. The second batch, indicated by the letter (B) after the sample number, was received as blocks measuring approximately 20 × 20 × 25 mm.

Potassium analyses on the first batch of samples were made at the Mineralogy Department of the Natural History Museum, London; argon analyses were then undertaken on the remaining powder. All analytical work on the second batch of samples was undertaken by the Isotope Geology Unit of the Institute of Geological Sciences (IGS).

In an attempt to reduce the atmospheric argon contamination, which can often be shown to be a function of fine grain size of the analyzed material, the second batch of samples was prepared for analysis by cutting into slices. Ten 1-mm-thick and five 2-mm-thick slices were cut from each block. Alternate 1-mm-thick slices were then selected to give two samples weighing approximately 5 g each which were finely crushed to give two powders for potassium analyses. Replicate K determinations indicated no significant difference in the potassium contents of the two samples prepared for each rock. Argon analyses were made on the thicker slices, each of which weighed about 1.5-2 g, which were broken into two or three fragments for loading into the vacuum system. These precautions brought about no improvement in the level of atmospheric argon contamination.

Analytical Methods, Precision, and Accuracy

Potassium was determined at the IGS laboratories by flame photometry using lithium as an internal standard. Replicate analyses indicated a pooled standard deviation of 2.5×10^{-3}. The precision obtained by the Natural History museum is not known to us, but we have considered it reasonable to adopt the value of $\pm 2.5 \times 10^{-3}$ for all the potassium determinations.

Argon was extracted by fusion in a bakable vacuum system. Samples were loaded and outgassed overnight at 150°C. Conventional clean-up procedures were used, i.e., Ti gathering, CuO trap at 550°C and liquid nitrogen cold trap. An argon-38 spike was introduced at the start of each fusion and the isotopic ratios $^{36}Ar:^{38}Ar$ and $^{40}Ar:^{38}Ar$ were measured in an AEI MS10 mass spectrometer operating in the static mode.

All the samples gave off copious amounts of H_2O, CO_2, and hydrocarbons, and clean-up proved difficult and time consuming. Atmospheric argon blanks were high, and if anything the finely ground samples gave better radiogenic yields than the sliced samples. Thus the nonradiogenic argon component would not appear to be due entirely to absorption of the atmospheric argon by finely powdered rock. The results would suggest the presence of nonradiogenic argon in the rock itself and raise the question of the validity of assuming an atmospheric $^{40}Ar:^{36}Ar$ ratio when correcting the argon yield for the nonradiogenic component.

Errors are given for the individual argon determinations and were calculated from the following equation:

$$\left[(\sigma\,\mathrm{sp})^2 + \left(\frac{\sqrt{(R_1)^2 + (A)^2 (R_2)^2}}{1 - A} \right)^2 \right]^{\frac{1}{2}}$$

where

- σ sp is the proportional error on the spike volume;
- R_1 is the proportional error on the measured ratio $^{40}Ar:^{33}Ar$;
- R_2 is the proportional error on the measured ratio $^{36}Ar:^{38}Ar$;
- A is the fractional amount of atmospheric argon.

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TABLE 1
K–Ar Data and Apparent Ages of Deep-Sea Basalt Samples

Sample	K (%)	Ar Ref.	Vol Range ^{40}Ar, cc/g	Rg(%)	Weighted Mean ^{40}Ar	Age (m.y.)
257-11-2	0.102	73.3	$4.771 \pm 0.774 \times 10^{-7}$	34		
	0.102	73.15	$4.110 \pm 0.438 \times 10^{-7}$	29	$4.3127 \pm 0.3504 \times 10^{-7}$	103 ±8
	0.102	73.20	$4.540 \pm 0.885 \times 10^{-7}$	39		
257-11-2 (B)	0.118	73.235	$4.338 \pm 0.395 \times 10^{-7}$	17	$4.463 \pm 0.2800 \times 10^{-7}$	92 ±7
	0.118	F 339	$4.537 \pm 0.408 \times 10^{-7}$	26		
257-13-3 (B)	0.051	F 275	$5.171 \pm 0.362 \times 10^{-7}$	11		
	0.051	F 338	$3.403 \pm 0.136 \times 10^{-7}$	22	$3.698 \pm 0.1214 \times 10^{-7}$	174 ±10
	0.051	F 346	$4.452 \pm 0.401 \times 10^{-7}$	8		
257-16-2 Plagioclase	0.026	73.38	$1.695 \pm 0.041 \times 10^{-7}$	10	$1.695 \pm 0.041 \times 10^{-7}$	157 ±5
257-17-5	0.066	73.16	$5.552 \pm 0.178 \times 10^{-7}$	29	$5.456 \pm 0.172 \times 10^{-7}$	196 ±9
	0.066	73.21	$4.607 \pm 0.645 \times 10^{-7}$	24		
257-17-5 (B)	0.065	73.282	$4.967 \pm 0.198 \times 10^{-7}$	22	$4.806 \pm 0.150 \times 10^{-7}$	177 ±9
	0.065	F 344	$4.592 \pm 0.230 \times 10^{-7}$	21		
250-26-6	0.47	73.1	$1.705 \pm 0.107 \times 10^{-6}$	36	$1.705 \pm 0.107 \times 10^{-6}$	89 ±6
251-31-4	0.102	73.31	$7.349 \pm 0.349 \times 10^{-7}$	7	$7.349 \pm 0.349 \times 10^{-7}$	39 ±2
253-58-1	0.124	73.28	$5.133 \pm 0.133 \times 10^{-7}$	18	$5.133 \pm 0.133 \times 10^{-7}$	101 ±3
254-35-1 (B)	0.177	73.234	$3.194 \pm 0.415 \times 10^{-7}$	15		
		F 344	$3.701 \pm 0.703 \times 10^{-7}$	10	$3.527 \pm 0.207 \times 10^{-7}$	49 ±5
		F 342	$3.629 \pm 0.253 \times 10^{-7}$	13		
254-36-3	0.309	73.30	$2.224 \pm 0.055 \times 10^{-7}$	24	$2.224 \pm 0.055 \times 10^{-7}$	18 ±0.5
256-10-2	0.195	73.33	$7.349 \pm 0.349 \times 10^{-7}$	54	$7.349 \pm 0.349 \times 10^{-7}$	92 ±4

Note: Decay constants: $\lambda_\beta 4.72 \times 10^{-10}$ yr^{-1}, λ_e 0.584×10^{-10} yr,$^{-1}$ ^{40}K:K = 0.0119%.

During the course of this investigation σ sp was between ±0.5% and ±1%, and R_1 was about ±0.2%. A typical value for R_2 is about ±1%, but in the present series of analyses difficulties in achieving good clean-up often resulted in appreciable tails to the argon-38 peaks giving rise to errors on the ^{36}Ar:^{38}Ar ratio of up to ±2%. In one particularly bad run (Sample 257-17-5, run 73.21) the error was ±4.5% resulting in an error on the volume of radiogenic argon of about ±17% when error magnification due to the correction for atmospheric argon was taken into account.

Where replicate argon analyses have been made, we have calculated a weighted mean and standard deviation, the individual determinations being weighted according to their calculated standard deviations.

Errors on the actual apparent ages have been determined by combining the errors on the potassium and argon determinations in the appropriate way. The proportional error on the age is of course slightly less than the proportional error on the radiogenic ^{40}Ar:^{40}K ratio.

More serious than the random errors discussed above is the possibility of systematic errors. The most obvious way in which such errors could arise is when poor clean-up results in tails to the 38 peak, which in turn make accurate determination of the background to the 36 peak difficult. A second cause of systematic error lies in the possibility that the nonradiogenic argon component may not have a normal present-day atmospheric argon ^{40}Ar:^{36}Ar ratio. The nonradiogenic argon could be made up of two components: (1) normal atmospheric argon-the apparatus blank; (2) extraneous argon derived from the sample. If the extraneous argon were entirely ^{40}Ar, then the radiogenic argon-40 calculated in the normal way (and hence the age) would be too high; this is the normal excess argon phenomenon. The amount of excess argon, however, could appear to vary in replicate analyses due to variation in the normal atmospheric argon contamination from analysis to analysis and possibly to heterogeneous distribution of excess argon in the sliced samples. If the sample also contained ^{36}Ar extraneous argon, it could not even be assumed that the radiogenic argon calculated in the normal way gave a maximum value, and again variation in the true atmospheric argon blank from run to run would give rise to poor reproducibility.

Thus extraneous argon presents something of an intractable problem, the effects of which cannot be easily assessed. Normal care was taken to minimize any systematic error due to interference of the 38 peak tail in the background determination at mass 36. Despite this, replicate argon determinations on Samples 257-13-3 and 257-17-5 yielded results which in the extreme differed by more than the sum of the appropriate standard deviations. This may imply the presence of extraneous argon.

Comments on Results

Sample 257-11-2 and 257-11-2(B)

Argon runs 73.3, 73.15, and 73.20 give results which agree within the limits of error. The age has been calculated from the weighted mean of the three argon determinations.

Sample 257-11-2(B) gives argon values which agree within the limits of error. The weighted mean of the two argon determinations has been used to calculate the age.

Although from the same segment of core the powdered (257-11-2) and sliced—257-11-2(B)—samples have significantly different K values. However, the two ages agree within error limits. The mean age 97 ±5 m.y. is Albian (Lambert, 1971, sets the base of the Cenomanian at 95 m.y.).

Sample 257-13-3(B)

The argon reproducibility is most unsatisfactory. Determinations F 275 and F 346 agree within the limits of error, but determination F 338 gives a result significantly lower. The high radiogenic argon value for F 338 results in a low standard deviation, and this determination dominates the weighted mean to give an age of 174 ±10 m.y.

The unweighted mean of the two higher argon determinations—F 275 and F 346— yields an age of 223 m.y. In relation to the age given by the overlying sample (257-11-2) and the underlying sample (257-17-5, 177 m.y. to 196 m.y.) an age of 223 m.y. would appear to be too high. We conclude that the age of 174 ±10 m.y. calculated from the weighted mean argon determination is the most satisfactory.

The poor reproducibility of these argon determinations may reflect a small amount of excess argon heterogeneously distributed in the rock, or may be due to sampling error which could well be enhanced by the low potassium content.

Samples 257-17-5 and 257-17-5(B)

The sliced sample (B) gives argon results which agree within limits of error but reproducibility for the powdered sample is very poor. The weighted mean for argon determinations 73.16 and 73.21 is strongly biased by the low error attached to determination 73.16. The very high error for determination 73.21 is due to an unusually high standard deviation on the ^{36}Ar:^{38}Ar ratio measurement.

We favor the age calculated for the sliced sample, 257-17-5(B) at 177 ±9 m.y., since this reflects the mean of two argon determinations which are in good agreement with each other and which are analytically satisfactory, as is indicated by low errors.

An age of 177 ±9 m.y. corresponds to the Lower Jurassic.

Sample 257-16-2

Plagioclase feldspar. A precise argon determination. The feldspar yields an age which is appropriately younger than the underlying basalt but also younger than the overlying rock. However, in view of the ambiguities associated with the determinations on the overlying basalt—257-13-3(B)—the discrepancies may not be particularly significant.

Sample 259-26-6

A satisfactory determination with a high content of radiogenic argon. A Cretaceous age, post-Cenomanian and pre-Campanian.

Sample 251-31-4

A late Eocene or early Oligocene age.

Sample 253-58-1

A Lower Cretaceous-Albian age.

Sample 254-35-1(B)

Good reproducibility of argon determinations. An Eocene age.

Sample 254-36-3

A Miocene age.

Sample 256-10-2

A Cretaceous-Cenomanian age.

DSDP SAMPLE 26-251A-29-1: POTASSIUM-ARGON AND FISSION TRACK DATING

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A split from this glassy basalt sample was dated by the conventional K-Ar method. Potassium concentrations were determined by flame photometry and argon concentrations by isotope dilution, using an Associated Electrical Industries MS10 mass spectrometer. The results are summarized below.

% K_2O (mean of 2 determinations) = 0.194;
Radiogenic ^{40}Ar content = 2.19×10^{-7} SCC/g;
% radiogenic ^{40}Ar = 73.9;
Apparent K-Ar age = 33.7 m.y.

An attempt also was made to date glass from the sample by the fission track method. The results are given below.

For the irradiated specimen:
Flux = 1.68×10^{17} nvt;
Fission track density = 54,380 ±1600 FT/cm^2;
Uranium content = 0.03 ppm (minimum).

For two unirradiated specimens:
No positively identifiable fission tracks were observed during a scan of 1 cm^2 of each sample.

Discussion

On the basis of fossil evidence, the sediments overlying this basalt sample are early Miocene (say about 20 m.y. old). The above K-Ar age therefore appears to be anomalously old. This probably is due to the presence of excess radiogenic argon, an interpretation reasonable in light of the substantial quantities of excess gas which have been observed in the glassy rims of submarine lavas from Hawaii (Dalrymple and Moore, 1968).

The fission track results are more difficult to interpret, the lack of tracks suggests an annealing. The form of the glassy basalt sample and the presence of concentric fractures in the glass indicate that it is an extrusion, not a sill. Furthermore, no baking of the sediment has been reported. If indeed, the sample is early Miocene in age, there should be close to 100 FT/cm^2 in the unirradiated specimen. Since none were observed (and the glass surface is excellent), we conclude that the glass has suffered annealing. This is somewhat difficult to understand since the temperature at the base of the sediment column in Hole 251A is probably less than about 25°C, a temperature which is probably too low to have resulted in significant annealing of tracks (Aumento, 1969). One possibility is that the glass was annealed during the drilling operation.

In conclusion, the age of the sea floor at this site is certainly less than 33.7 m.y. and probably is in the range 20-30 m.y.

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