30. K-Ar AND ^{40}Ar-^{39}Ar DATING OF SITE 319 AND 321 BASALTS

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INTRODUCTION

The use of K-Ar age determinations in deep-sea basalts has been inhibited by uncertainties resulting from low temperature alteration (Hart, 1970) and the possibility of trapped argon due to the rapid quench under high hydrostatic pressures (Dalrymple and Moore, 1968). The ^{40}Ar-^{39}Ar variation of K-Ar dating offers some hope of obtaining more reliable ages from deep-sea basalts, particularly when the sample is analyzed using the incremental heating mode.

In this procedure a sample that has been irradiated by fast neutrons is heated at various temperature intervals, and the ^{40}Ar and ^{39}Ar produced primarily from n-p reaction with ^{39}K are analyzed. For samples with no initial argon and no loss of argon or gain of potassium, the ages calculated from each temperature increment should be the same and equal to the total fusion K-Ar age, which in this case would be valid. Late addition of K by low temperature alteration or loss of Ar by diffusion, however, will give discordant age results for the different temperature fractions. The ^{40}Ar-^{39}Ar incremental heating analysis is amenable to evaluation by isochron construction as well. By this procedure the data from individual heating steps are plotted on an $^{40}Ar/^{36}Ar$ versus $^{39}Ar/^{36}Ar$ diagram. The slope of the line through the points is proportional to the age, and the intercept is a measure of the initial $^{40}Ar/^{36}Ar$ value. This form of data evaluation is useful for deep-sea basalts because there are no assumptions concerning the initial $^{40}Ar/^{36}Ar$ value, and valid ages can be obtained from samples containing trapped initial argon.

In this paper we have attempted to date the basement in Hole 319A and Site 321 by using both the traditional K-Ar and the ^{40}Ar-^{39}Ar techniques.

One sample from Hole 319A (7-1, 105-109 cm) and two from Site 321 (14-1, 45-47 cm; 14-4, 58-60 cm) were chosen for analysis. The samples are relatively unaltered for deep-sea basalts. The thin-section examination showed that a greenish-brown phase tentatively described as "smectite" occupies from 10% to 15% of the rock from Sample 319A-7-1, 105-109 cm and is found in small vugs, along grain boundaries, and as an olivine replacement. Sample 321-14-1, 45-47 cm appeared least altered in thin section. Minor amounts of brown and green smectite are found throughout the sample. Sample 321-14-4, 58-60 cm has some brown-colored alteration along the edges of the feldspars and rare vugs containing brown smectite.

EXPERIMENTAL PROCEDURES

Each of the samples was crushed, washed in distilled water, dried, and sieved to give particles ranging in size from 20 to 50 mesh. After the samples were prepared in this fashion, each was placed in a vial of high purity fused silica and the capsules evacuated and sealed.

The 16 samples which make up an irradiation are divided into four groups, each of which contains three samples whose age is to be determined, and one standard. In order to minimize the effects of vertical neutron flux gradients, the center of each specimen within each group is aligned in a common horizontal plane.

The samples are placed in the central thimble of the Oregon State University Radiation Center's Triga reactor and irradiated for 4 hr at 1 mw which exposes the samples to an integrated epithermal flux of $10^{18}n/cm^2$. At the end of the irradiation period, the samples are stored for approximately one month so that short half-lived isotopes can decay to negligible intensity levels, but any ^{37}Ar will have decayed by less than half.

In order to extract its gases, each sample is removed from its fused silica vial and placed in a molybdenum-tantalum crucible which in turn is put into the gas extraction system which, after bakeout, is maintained at approximately 10^{-8}torr. The samples are baked for approximately 10 hr at 160° to 200°C after which the gases are extracted by induction heating for 40 min at various temperature intervals. The temperatures are measured with a tungsten, tungsten-rhenium thermocouple placed at the sample. The reactive gases given up by the sample are removed by hot titanium getters before the argon isotopic ratios are measured.

The argon isotopic ratios relative to mass 40 are measured using a Reynolds-type mass spectrometer fitted with an ion multiplier. The analog signals are converted to digital data and recorded on paper tape for computer processing.

The results of the stepwise gas extractions from each of the three samples discussed in this report are shown in Table 1. The data plotted in Figures 1, 2, and 3 are taken from this table. Each figure shows, not only an isochron age, but also a plot of the apparent age of each temperature increment versus the cumulative fraction of $^{39}Ar^{NK}$ released.

The age for each temperature step was determined using the method of Brereton (1970) with the relative argon isotope production constants determined for the Triga reactor using fused and degassed fluorite and wollastonite for calcium and kalsilite for potassium. The coordinates, "$^{40}Ar/^{36}Ar$ corrected" and "$^{39}Ar/^{36}Ar$ corrected," used to determine the isochron age are calculated also using Brereton's (1972) method. The age is then determined from a weighted linear regression upon these points (Bevington, 1969). All the computations are done by computer.

RESULTS

Let us define an "ideal rock" as one having the following properties: (1) the only contamination is air, (2) the rock has been subjected to no weathering, (3) no gas has been lost, and (4) the argon concentration held

TABLE 1
Age Data

Sample (Interval in cm)	Heat Step	%K	$^{40}Ar_R$ (10^{-8} cc/g)	$\%^{40}Ar_R$	$\left.\frac{^{40}Ar}{^{36}Ar}\right\|_c$	$\left.\frac{^{39}Ar}{^{36}Ar}\right\|_c$	$\%^{39}Ar_t$	Age (m.y.)	Prec.[a] (m.y.)
319A-7-1, 105-109	400°C		2.36	1.94	301.36	1.055	62	10.92	1.01
	500°C		1.07	4.83	310.49	1.752	18	16.81	0.89
	700°C		1.17	6.25	315.17	2.357	20	16.41	0.60
	K-Ar	0.1331	4.36	2.16				8.17	1.55
	Isochron age (15.2 ±3.6 m.y.), intercept 296.9 ±3.9								
321-14-4, 58-60	400°C		2.12	3.88	307.4	0.6642	17	38.9	2.25
	500°C		4.29	32.2	435.7	7.020	30	43.1	1.20
	700°C		6.44	44.0	527.8	11.51	45	43.6	1.05
	Fusion		0.77	5.91	314.1	1.435	8	28.0	3.04
	Isochron age (43.7 ±1.2 m.y.), intercept 293.2 ±0.7								
321-14-1, 45-47	400°C		0.871	1.56	300.2	0.9072	29	8.51	0.10
	500°C		0.977	3.25	305.4	1.492	25	10.9	0.72
	700°C		2.50	15.9	351.5	3.885	30	23.6	0.34
	900°C		1.76	7.12	318.2	1.259	16	29.5	1.83
	K-Ar	0.1278	11.95	7.16				22.9	1.27
	Isochron age (27.8 ±0.5 m.y.), intercept 284.8 ±0.2								

[a]The precision listed is for 1 standard deviation.

in the rock after activation may be described for each extraction increment by the same isochron equation.

$$\left.\frac{^{40}Ar}{^{36}Ar}\right|_c = \left(\frac{^{40}Ar}{^{36}Ar}\right)^{at} + R\left.\frac{^{39}Ar}{^{36}Ar}\right|_c$$

where the subscript c refers to the argon isotopic ratios corrected for calcium and potassium interferences, R is a constant depending only upon the age of the rock, and $(^{40}Ar/^{36}Ar)^{at}$ is the atmospheric argon contamination ratio. For this ideal rock a plot of apparent ^{40}Ar-^{39}Ar age versus the cumulative fraction of ^{39}Ar released would be a horizontal line with each extraction having the same apparent age equal to that of the isochron age.

Figure 1 shows both an isochron plot and a cumulative fraction of ^{39}Ar versus apparent age plot for the Hole 319A basalt taken from the depth interval 105-109 cm. It is seen that this sample cannot be classed as "ideal" since the 400°C extraction increment has an apparent age which is approximately 30% lower than those of the 500° and 700°C steps. The isochron age determined from all three steps is nearly 25% higher than the apparent age of the 500° and 700°C increments. The intercept which ideally should be 295.5 is 290.3 ±1.2.

The departure from the ideal of the sample from Hole 319A may best be explained by low temperature weathering which results in the uptake of potassium by weathering products during the time interval between the initial cooling of the rock and the present. The potassium-bearing alteration phases give rise to argon, but may not retain it so that the total radiogenic ^{40}Ar is composed of two parts, one associated with the initial potassium and the other with the acquired potassium, diminished by any argon losses. The ^{39}Ar, however, is associated with the total potassium. Thus, the ratio of

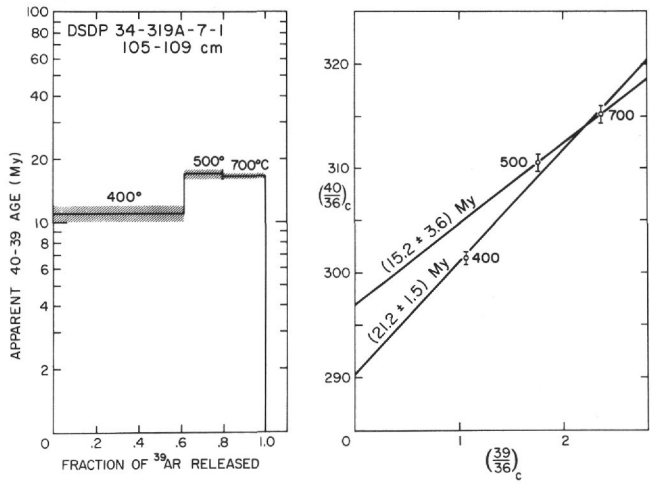

Figure 1. *Plot of apparent ^{40}Ar-^{39}Ar age versus fraction of ^{39}Ar released and ^{40}Ar-^{39}Ar isochron for Sample 319A-7-1, 105-109 cm. The shaded areas represent one standard deviation for the apparent ages.*

the radiogenic ^{40}Ar to ^{39}Ar in the lowest temperature fraction reflects, not only the addition of potassium, but also the loss of radiogenic ^{40}Ar which can result in an apparent age that is lower than those determined from the higher temperature releases. Extremely altered fine-grained basalts have been shown to lose ^{39}Ar preferentially to ^{40}Ar (Seidemann, 1974) because of radiation damage; however, this behavior predicts an increase in the $^{40}Ar^*/^{39}Ar$ ratio and hence a larger apparent age. The term $^{40}Ar^*$ represents radiogenic ^{40}Ar.

The relative amounts of alteration between the three samples which were analyzed appear to be reflected in the water contents presented in Table 2. Sample 319A-7-

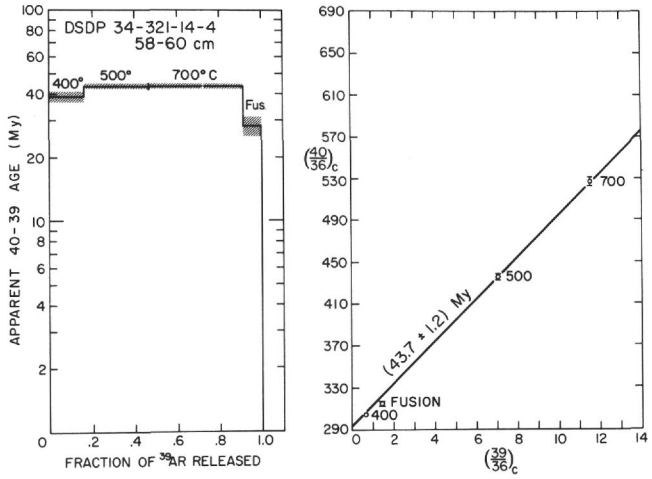

Figure 2. *Plot of apparent ^{40}Ar-^{39}Ar age versus fraction of ^{39}Ar released and ^{40}Ar-^{39}Ar isochron for Sample 321-14-1, 58-60 cm. The shaded areas represent one standard deviation for the apparent ages.*

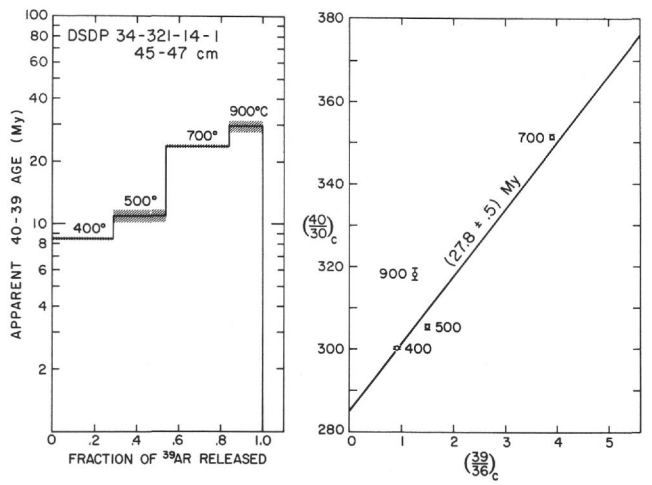

Figure 3. *Plot of apparent ^{40}Ar-^{39}Ar age versus fraction of ^{39}Ar released and ^{40}Ar-^{39}Ar isochron for Sample 321-14-1, 45-47 cm. The shaded areas represent one standard deviation for the apparent ages.*

TABLE 2
Water and Potassium Contents of Dated Samples

Sample (Interval in cm)	H_2O^-[a] (%)	H_2O^+[b] (%)	Total H_2O (%)	Potassium (%)
319A-7-1, 105-109	1.17	0.86	2.03	0.128
321-14-1, 45-47	0.43	0.34	0.77	0.134
321-14-4, 58-60	1.09	0.55	1.64	0.120

[a] H_2O^- is defined as the water removed by heating for 1 hr at 110°C

[b] H_2O^+ is defined as the water removed at temperatures greater than 110°C.

All water measurements were determined with a Dupont 26-321A-MA moisture analyzer.

1, 105-109 cm with 2.03% water is the most altered. In view of the degree of alteration, the low value of the 400°C apparent age, and the intuitive idea that argon from the loosely held extraneous potassium will be purged at low temperatures, we have constructed an isochron (Figure 1) for this sample from the 500° and 700°C temperature fractions which have apparent ages of 16.8 ±0.9 m.y. and 16.4 ±0.6 m.y., respectively. The age calculated from the slope of this line is 15.2 ±3.6 m.y. and the intercept is 296.9 ±3.9, the air ratio within experimental error. In contrast to the K-Ar age for this sample which is 8.17 ±1.55 m.y., the $^{40}Ar/^{39}Ar$ isochron age and the age plateau formed by the 500° and 700°C heatings are in good agreement with the age inferred from the delimiting, overlying sediments designated as the N8 planktonic foraminiferal zone. This zone, according to the Berggren (1972) time scale, is 16-16.7 m.y.

The age data from the stratigraphically lower of the two samples from Sample 321-14-4, 58-60 cm are shown in Figure 2. Judging from the cumulative fraction of ^{39}Ar versus apparent age plot, this sample appears to be a nearly ideal rock. Thin-section examination shows only a small amount of weathered phases, and, while the 400°C heating fraction exhibits a slightly lower apparent age than the 500° and 700°C increments, the difference is hardly significant. Thus, there appears to be little if any potassium uptake and/or radiogenic ^{40}Ar loss. The last heating step in which the sample was fused gave a significantly lower age which may reflect fractionation of the small amount of ^{39}Ar left in the sample.

The $^{40}Ar/^{39}Ar$ isochron, also shown in Figure 2, yields an age of 43.7 ±1.2 m.y. and an intercept of 293.2 ±0.7. If the fusion step is omitted, then the age is 43.8 ±1.2 m.y. and the intercept is equal to 294.0 ±0.7.

Both these isochron ages and the age plateau in the age spectrum plot (Figure 2) are in good agreement with that inferred from the overlying sediments, which are the P16 planktonic foraminifera zone. According to the Berggren (1972) time scale, this zone is 38 to 41 m.y.

Sample 321-14-1, 45-47 cm appears to be the least altered on the basis of the water content and thin-section examination. The isochron shown in Figure 3, which has been constructed from the scattered data presented there, yields an age of 27.8 ±0.5 m.y. in fair agreement with the K-Ar age (22.9 ±1.3 m.y.). The apparent age versus cumulative fraction of ^{39}Ar plot shown for this sample in Figure 3 indicates that it is not an ideal rock by any means; no two heating steps have the same apparent age. All of these ages are at least 25% lower than the 40-m.y. age of the overlying sediments which are in agreement with magnetic data for this site.

This sample is very puzzling! The traditional K-Ar age (22.9 m.y.) is only half that determined for the other sample from the same hole and from magnetic data and the paleontologic age of the overlying sediments. Low-temperature weathering and/or argon loss can account for both the low traditional K-Ar age and the age spectrum shown in Figure 3. The puzzle, however, arises as to how the $^{40}Ar/^{39}Ar$ and K-Ar data can be reconciled with the low water content and minor alteration visible in thin section. Possibly the potassium in the particular sample is located in poorly crystalline phases along

grain boundaries so that diffusive loss of radiogenic argon has resulted in a low age without obvious weathering. Alternatively, the minor quantity of weathering phases in this sample may have relatively higher potassium contents than other samples which appear more weathered. The weathering phases are poorly defined as to petrogenesis, composition, and structure. Until we can more accurately identify these phases and know more about their chemical composition, their effects on the bulk chemistry of the rocks and measured K-Ar ages will remain obscure.

From our results it appears that two of the three samples dated by the ^{40}Ar-^{39}Ar method yield useful age information. For Hole 319A the agreement between the isochron age determined from the 500° and 700°C extractions of 319A-7-1 (15.2 ±3.6 m.y.), the apparent ages of the 500° and 700°C heatings themselves (approximately 16.6 m.y.), and the biostratigraphic age (16-16.7 m.y.) strongly suggests that the basement rocks are not sills intruded into the sediment. It is possible that these ages mark the true basement age for this site although the magnetic anomaly data of Herron (1972) suggest an age of >20 m.y. Because the anomaly data in this region are generally poor, the tentative placement of anomaly 6 to the east of Site 319 is possibly in error. For Site 321, the agreement between the isochron age (43.7 ±1.2 m.y.), the age spectrum plateau (41.9 m.y.), the biostratigraphic age (38-41 m.y.), and the magnetic anomaly age (approximately 39 m.y.) strongly indicates that the basalts represent mid-ocean ridge volcanism rather than off-ridge sills.

On the basis of these limited data, it appears that the ^{40}Ar-^{39}Ar dating technique has the potential to determine correct ages even for samples that have experienced minor weathering, weathering that would obscure the conventional K-Ar age.

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