20. AGE DETERMINATIONS ON IGNEOUS ROCKS IN HOLE 373A

20.1. POTASSIUM-ARGON AGE DETERMINATION OF BASALT SAMPLES FROM LEG 42A, HOLE 373A, CORE 7

H. Kreuzer, M. Mohr, and I. Wendt, Bundesanstalt für Geowissenschaften und Rohstoffe, Hannover, West Germany

ABSTRACT

Eight basalt samples from Sections 2, 4, and 5 of Core 7, DSDP Hole 373A, were investigated petrographically and chemically in order to determine their suitability for potassium-argon dating. All of the samples were at least partially altered, and thus partial loss of argon may have occurred. Close to the lower boundary of the sampled interval the basalt shows petrographic and chemical indications of a higher degree of alteration. Here the potassium-argon dates are around 3.5 million years while in central parts of the interval the dates are around 5 million years. Consideration of the petrographic and chemical analyses together with K/Ar dating results in a minimum age determination for this interval of 4 million years.

INTRODUCTION

During Leg 42A of the Deep Sea Drilling Project, a site was drilled on the flank of a seamount on the Tyrrhenian Abyssal Plain (latitude 39° 43.68′N, longitude 12°59.56′E) in a water depth of 3517 meters. A 270-meter-thick Pliocene to Quaternary sequence of marls, tuffs, and zeolitic sediments was penetrated before drilling reached the acoustic basement. Penetration into this basement reached a total of 187.5 meters. The sequence comprised: an upper 30 meters of basaltic breccia with a limestone matrix, approximately 105 meters of porphyritic and amygdular basalts interlayered with basaltic breccia, and these were followed downwards by aphyric basalts flows to a terminal depth of 457.5 meters subbottom.

Eight samples were received at this laboratory for potassium-argon dating. These were taken from Core 7 within the interlayered sequence of basalt and basalt breccia. The core itself contains only an upper 50 cm of basaltic breccia while the remainder (approximately 5 m) is entirely made up of basalt with inclusions of palagonite and tuffaceous sediment or veins of sparry calcite.

METHODS

Each sample was initially subjected to detailed petrographic and chemical analysis in order to assess alteration and thus the degree of accuracy to be expected from the dating technique. In particular, we wished to determine the likelihood of argon loss through alteration of the basalt.

The K/Ar dating was carried out on whole-rock samples. These were ground to less than 800 μm, treated with 10% formic acid for 4.5 hours to remove calcite, soaked overnight in 0.4 N sodiumpyrophosphate solution, and intensively treated ultrasonically (after dilution to 0.01N) to remove weakly attached particles. Afterwards the samples were washed with distilled water and menthanol and dried at 50°C. Argon was determined by isotope dilution and potassium by flame photometry. The relative analytical error of the potassium determination (approximately ±2%) is negligible compared with the large error of the radiogenic argon concentration. This is due to the small absolute amount and the correspondingly low fraction of radiogenic argon in the total argon.

PETROGRAPHY

The upper five samples of the sequence show no marked petrographic differences. Table 1 lists our general petrographic observations derived from the microscopic analyses and serves to distinguish an upper group of five porphyritic, amygdaloidal basalt samples from three altered types of varying texture which make up the bottom of the sequence.

In the upper five samples plagioclase phenocrysts are generally free of alteration, but the laths of the groundmass may show strong alteration to carbonate. Augite phenocrysts have suffered alteration of varying intensity to smectite, with the smectite growth beginning at the grain boundaries. Olivine phenocrysts are generally completely altered to a mixture of limonite, smectite, and carbonate. However, in Samples 7-2, 17-25 cm, and 7-4, 0-9 cm, isolated crystal shapes are present containing relic unaltered olivine. Olivine is believed also to have been part of the groundmass in these rocks, but is not identifiable because of the level of alteration. Smectite limonite aggregates occur in any interstices which are not filled with pyroxenes. Sample 7-2, 34-41 cm, is especially rich in limonite. It is generally impossible to determine whether this mineral has formed during late-stage development of a smectite-limonite mixture as an interstitial filling or whether it is simply an alteration product of mafic minerals. Amygdules are usually coated with smectite and filled with carbonate.

Alteration extends even to the larger phenocrysts in Sample 7-4, 74-83 cm. Plagioclase phenocrysts up to 1 mm long, with the exception of their rims, are entirely

TABLE 1
General Petrographic Observations on Basalt Samples From Hole 373A, Core 7

Sample (Interval in cm)	Texture	Notes on Minerals Present						Rock Name
		Plagioclase	Augite	Olivine	Opaques	Carbonate	Smectite	
7-2, 17-25	Porphyritic, amygdaloidal; groundmass intergranular to intersertal; amygdules generally <2 mm length	As phenocrysts: single or agglomerated, idiomorphic morphic, tabular; An $\sim$80%, zoned or twinned, up to 5 mm length In groundmass: laths, twinned or zoned	Hypidiomorphic, in groundmass between plagioclase laths, light brown, zoned, or mosaic structure, 0.05-0.3 mm length	Stout phenocrysts; idiomorphic, up to 2 mm length; probably in groundmass also	Skeletal grains as inclusions in augite and smectite	Generally present	Aggregates in interstices	Porphyritic amygdaloid basalt
7-2, 34-41							Very rich in smectite/ limonite aggregates	
7-2, 131-136				Idiomorphic phenocrysts, reduced size; probably in groundmass also			Interstitial filling, very fine grained aggregates or subparallel fibers, 0.1 mm long.	
7-2, 142-150				Phenocrysts idiomorphic, up to 2 mm length; probably in groundmass also				
7-4, 0-9								
7-4, 74-83	Porphyritic, amygdaloidal; groundmass intersertal to subophitic	Few stout, tabular, altered, idiomorphic phenocrysts, up to 1 mm length; An $\sim$80%; laths in groundmass 0.1 to 0.4 mm length	Hypidiomorphic to xenomorphic; lightish brown, zoned or mosaic structure, 0.1-0.4 mm length	Few altered phenocrysts, 1-3 mm	Idiomorphic grains, evenly distributed, mainly as inclusions in smectite	Present in interstices between plagioclase laths of groundmass	Fine-grained smectite aggregates, fibers rare green color	Porphyritic amygdaloidal basalt (altered)
7-4, 136-141	Aphyric, subparallel; Amygdules 0.5 mm length; 2 zones, 1 mm wide, show of coarsening matrix	Laths in groundmass, 0.05-0.2 mm length; one altered microphenocryst (0.3 mm long); some orientation	Hypidiomorphic to xenomorphic; light brown (Ti rich?), zoned or mosaic structure		As inclusions in augite	Plagioclase laths altered to carbonate	Smectite as inclusions in plagioclase laths	Fine-grained amygdaloidal basalt (altered)
7-5, 0-7	Fine to extremely fine grained, partly microlitic	Acicular, partly skeletal, 0.05 to 0.1 mm length	Hypidiomorphic (?), highly altered; brownish, up to 1 mm length	Idiomorphic, 0.6 mm length; highly altered	Limonite present	As veins 0.5 mm broad	Smectite as inclusions in plagioclase laths	Fine-grained amygdaloidal basalt (strongly altered)

replaced by carbonate. Plagioclase laths in the matrix of this sample are generally penetrated by smectite and carbonate which also occur as interstitial filling. The rims of augite phenocrysts are frequently altered to smectite and the few larger (1-3 mm) olivine phenocrysts are completely altered to limonite, smectite, and carbonate. Smectite also occurs as cross-laminated aggregates and sometimes as parallel fibers (0.1 mm long) which may have formerly been pyroxenes. The matrix smectite in this sample frequently contains fine-grained leucoxene which may suggest a former glassy groundmass.

Plagioclase laths in the fine-grained amygdaloidal basalt sample, 7-4, 136-141 cm, contain inclusions of smectite which again might have formed by alteration or devitrification of glassy matrix inclusions. Augite crystals in the groundmass are partially altered to smectite, and the latter also fills most of the interstices between these and the plagioclase laths. The amygdules present are coated with smectite and filled with carbonate.

In the most altered and lowermost sample, 7-5, 0-7 cm, plagioclase laths usually contain smectite, and both augite and olivine are almost entirely replaced by a mixture of smectite and limonite. The groundmass consists of smectite with limonite and small idiomorphic ore grains. Pseudomorphs after mafic minerals are difficult to recognize. Amygdules in this sample, up to 0.5 mm long, are again filled with carbonate.

CHEMICAL ANALYSIS

The results of the chemical analyses (X-ray fluorescence, H_2O, FeO, CO_2 = wet chemical analyses) are shown in Table 2, with those for trace elements in Table 3. These chemical analyses agree rather well with the results obtained by Dietrich et al. (this volume), especially if one compares the average values they report for samples from Core 7 with the averages of our results.

As can be seen in Table 2, the five samples from the upper part of Core 7 have significantly higher SiO_2 and Al_2O_3, and slightly higher K_2O and Na_2O concentrations than the three samples closest to the base. However, MnO, MgO, and FeO(?), as well as H_2O and CO_2, are all significantly lower in the samples of the upper group of five samples.

The lower SiO_2, Al_2O_3, and alkali concentrations (including the trace element Sr) in the lower parts of the sampled sequence correspond with an absence of plagioclase phenocrysts as reported in the petrography section. The increase in MgO (and also Mn and V, Table 3) in these samples suggests a relative enrichment in mafic components (see Figure 1). However, because of the strong alteration detectable in these samples, it is not possible to determine whether olivine or enstatite (resp. pigeonite) could be responsible for this increase.

Trace elements which are resistant to alteration, such as Zr, Nb, Y, and Sc, appear in both groups. In the Ti-Y-Zr triangle-plot from Table 3 all of the samples are located in the "Ocean-Floor-Basalt" (OFB) area (Figure 2).

Table 4 shows the CIPW-normative composition of the samples as calculated from the chemical analyses in Table 2. The resulting plagioclase plot (Figure 3) yields an An content of about 55% to 65% (except for Sample 7-5, 0-7 cm, which is close to the base of the core). Again this is in agreement with the results of Dietrich et al. (this volume). However, in contrast, our calculated hypersthene contents are generally higher, and the olivine contents (Figure 4) are lower than those given by these workers. All of the samples plot in the olivine tholeiite field.

SUITABILITY OF THE CORE 7 SAMPLES FOR K/AR DATING

Petrographically we recognize the eight samples as having come from the central part (the upper group of five) and lower margin (the lower three) of a basaltic sill. The rock is classified as an amygdaloidal basalt, its main constituents being plagioclase (phenocrysts and matrix), augite and smectite, with minor olivine (phe-

TABLE 2
Chemical Analysis of Samples From Hole 373A, Core 7 (in %)

	7-2, 17-25 cm	7-2, 34-41 cm	7-2, 131-136 cm	7-2, 142-150 cm	7-4, 0-9 cm	7-4, 74-83 cm	7-4, 136-141 cm	7-5, 0-7 cm
SiO_2	46.87	47.81	48.36	47.07	46.29	45.10	44.42	41.41
Al_2O_3	18.74	18.56	18.93	18.71	18.83	17.01	16.68	16.24
TiO_2	0.874	0.915	0.930	0.844	0.827	0.882	0.957	0.893
Fe_2O_3	4.97	5.50	4.77	5.09	4.75	4.90	5.46	4.87
FeO	2.55	2.55	2.41	2.48	2.71	3.31	3.09	3.43
MgO	8.02	7.63	7.49	7.95	8.39	10.15	10.07	11.14
CaO	10.43	10.09	10.25	10.52	10.70	9.99	10.66	10.59
MnO	0.108	0.103	0.091	0.108	0.114	0.133	0.176	0.178
Na_2O	2.95	2.99	3.05	2.81	2.68	2.58	2.57	2.37
K_2O	0.30	0.37	0.33	0.27	0.23	0.26	0.22	0.25
P_2O_5	0.12	0.13	0.12	0.10	0.10	0.10	0.11	0.11
SO_3	0.02	0.01	0.02	0.03	0.11	0.03	0.05	0.82
CO_2	<0.03	0.14	0.06	0.21	0.42	0.88	0.89	1.53
H_2O	3.24	2.80	1.63	3.60	3.97	4.62	3.99	4.86
LOI	0.33	0.53	1.60	0.24	−0.04	0.76	1.07	2.57
Total	99.55	100.13	100.04	100.03	100.08	100.71	100.41	101.26

TABLE 3
Trace Elements of Samples From Hole 373A, Core 7 (in ppm)

	7-2, 17-25 cm	7-2, 34-41 cm	7-2, 131-136 cm	7-2, 142-150 cm	7-4, 0-9 cm	7-4, 74-83 cm	7-4, 136-141 cm	7-5, 0-7 cm
Sr	212	201	210	214	211	190	190	175
Rb	12	10	3	14	4	8	7	12
Nb	5	4	4	1	0	2	5	2
Zr	72	78	78	68	61	66	69	65
Y	21	35	27	21	34	25	21	23
Pb	14	27	10	18	12	11	23	5
Ni	84	112	100	88	97	140	92	102
Co	36	30	35	31	36	42	41	40
Mn	862	831	732	879	900	1060	1440	1474
V	148	150	151	149	152	161	177	163
Zn	47	61	51	49	47	60	73	81
Cu	81	85	70	78	59	73	129	196
Cr	274	259	273	279	311	270	236	240
Ce	30	30	16	26	27	23	35	25
La	5	1	2	4	0	0	0	2
Ba	70	99	80	82	74	93	86	75
Sc	32	33	33	37	38	35	38	37

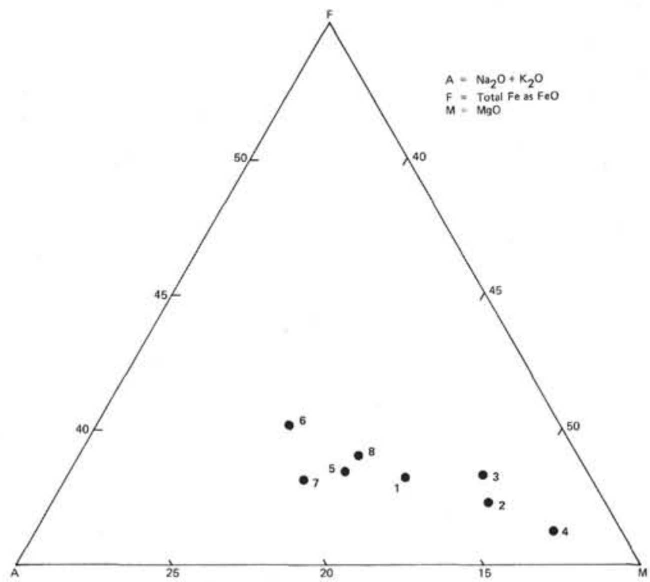

Figure 1. *A-F-M plot of Core 7 basalt samples. Key to sample numbers: 1 = 7-4, 0-9 cm; 2 = 7-4, 74-83 cm; 3 = 7-4, 136-141 cm; 4 = 7-5, 0-7 cm; 5 = 7-2, 17-25 cm; 6 = 7-2, 34-41 cm; 7 = 7-2, 131-136 cm; 8 = 7-2, 141-150 cm.*

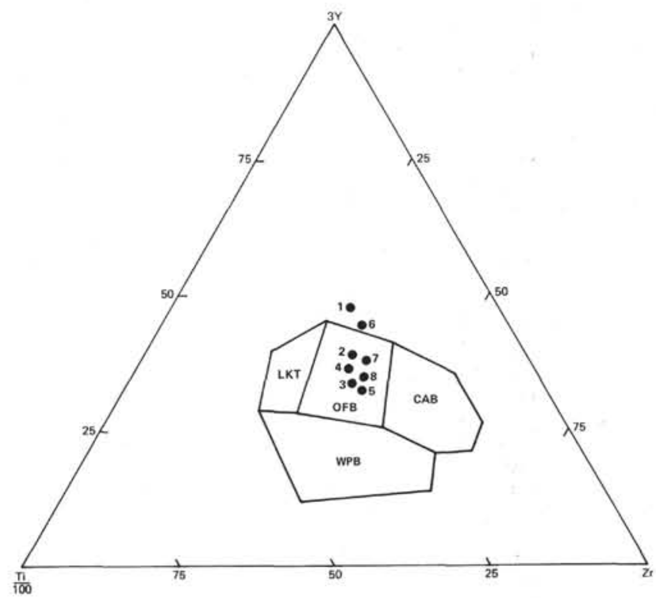

Figure 2. *Ti-Zr-Y triangle plot of Core 7 samples. LKT = low potassium tholeiite; OFB = ocean floor basalt; CAB = calc alkali basalt; WPB = within plate basalt. (Sample numbers same as in Figure 1.)*

nocrysts and ground mass), opaques (including limonite), and carbonate. Sporadically, pigeonite and quartz are identifiable. The phenocryst content decreases to zero towards the lower selvage while smectite and carbonate increase due to the alteration of plagioclase and mafic minerals. The mafites may also be partially altered in the central parts of the sill.

Samples 7-4, 74-83 cm; 7-4, 136-141 cm; and 7-5, 0-7 cm; are consequently unsuitable for dating because of intense alteration whereas the other five samples appear moderately suitable for radiometric dating on the basis of their petrography.

Chemically, few of the samples are sufficiently fresh for confident dating. Generally water contents are less than 2%. The three samples from the lower part of the basalt layer (7-4, 74-83 cm; 7-4, 136-141 cm; 7-5, 0-7 cm), which on petrographic grounds are already unsuitable for K/Ar dating, have the highest H_2O contents. SiO_2 and H_2O (Figure 5) as well as TiO_2 (Figure 6) and H_2O, are negatively correlated for the upper five samples, while the lower three samples deviate considerably from the regression lines defined by the upper group. On the other hand, the degree of oxidation (Fe^{3+}/Fe_{total}) is negatively correlated with H_2O (Figure 7).

POTASSIUM-ARGON DATING RESULTS

The radiometric dating results are listed in Table 5. The ages of the eight samples range from 3 to 5 m.y.

TABLE 4
CIPW – Normative Composition of Hole 373A Core 7 Samples (degree of oxidation as determined)

	7-2, 17-25	7-2, 34-41	7-2, 131-136	7-2, 142-150	7-4, 0-9	7-4, 74-83	7-4, 136-141	7-5, 0-7
Or	1.79	2.19	1.98	1.60	1.36	1.54	1.31	1.50
Ab	25.03	25.34	26.08	23.63	21.93	21.65	21.56	14.88
An	37.37	36.31	37.64	37.82	39.01	34.19	33.72	36.26
Ne	–	–	–	HM(1.01)	–	–	–	–
Di	10.74	9.50	9.99	9.72	8.336	7.17	10.21	5.04
Wo	5.76	5.10	5.36	5.21	4.472	3.83	5.48	2.69
En	4.98	4.40	4.63	4.51	3.862	3.23	4.74	2.25
Fs	–	–	–	–	–	0.10	–	0.09
Hy	7.49	12.75	12.79	11.92	12.42	12.64	8.93	14.64
En	7.49	12.75	12.79	11.92	12.42	12.24	8.93	14.06
Fs	–	–	–	–	–	0.40	–	0.58
Ol	5.36	1.34	1.07	2.39	3.21	7.13	8.11	8.64
Fo	5.36	1.34	1.07	2.39	3.21	6.88	8.11	8.27
Fa	–	–	–	–	–	0.25	–	0.37
Mt	6.10	5.90	5.45	5.93	6.68	7.109	7.81	7.15
Il	1.66	1.75	1.79	1.60	1.57	1.67	1.83	1.71
Ap	0.29	0.31	0.29	0.24	0.237	0.24	0.26	0.26
Th	0.04	0.02	0.04	0.05	0.195	0.05	0.09	1.47
Hm	0.80	1.45	1.09	1.01	0.138	–	–	–
Cc	0.07	0.32	0.14	0.48	0.954	2.00	2.04	3.53
H_2O	3.24	2.80	1.63	3.60	3.97	4.62	3.99	4.86
Total	100.01	99.98	99.98	99.99	100.00	100.01	99.98	99.94

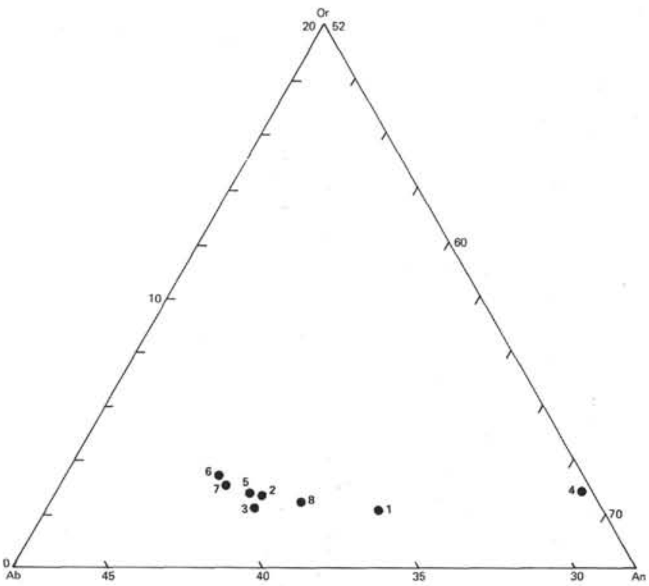

Figure 3. *Normative plagioclase (Or, Ab, An) plot of Core 7 samples. (Sample numbers same as in Figure 1.)*

with individual errors of 20% to 50%. The lowest ages correspond to the most altered samples in the lower part of the sampled sequence (i.e., the lower margin of the sill). They yield an average age of 3.4±0.5 m.y. while the less altered upper group of five samples yield an average age of 4.2±0.5 m.y., and a weighted mean age of 4.0±0.3 m.y.

DISCUSSION

The average deviation from the weighted mean age quoted above exceeds the mean analytical error (1.6σ), so there is evidence here for disturbance of the K/Ar system. This is indeed likely in view of the alteration detected in all of the samples. Thus we regard the K/Ar dates of Table 5 as minimum ages. The basalt of Core 7 consequently should be older than 4.0 ±0.3 m.y.

Savelli and Lippanni (this volume) analyzed two samples from Core 7. Their samples from Section 2 (5-12 cm and 67-76 cm) are from the vicinity of our samples in that section (17-25 cm, 34-41 cm, and 131-136 cm). However, their K/Ar ages are significantly higher than ours (mean age 7.2 ±0.9 [2σ] m.y.). It is possible that the formic acid, sodium phosphate, and ultrasonic treatments applied in our laboratory are capable themselves of reducing K/Ar ages and this is to be checked.

ACKNOWLEDGMENTS

We wish to thank Prof. Harre and Dr. Raschka and their laboratory staff for the chemical analyses, and Dr. P. Müller for critical and stimulating discussion of our results.

REFERENCE

Harland, W. B. and Francis, E. H. (Eds.), 1971. The Phanerozoic time scale: Geol. Soc. Lond. Spec. Publ., v. 5.

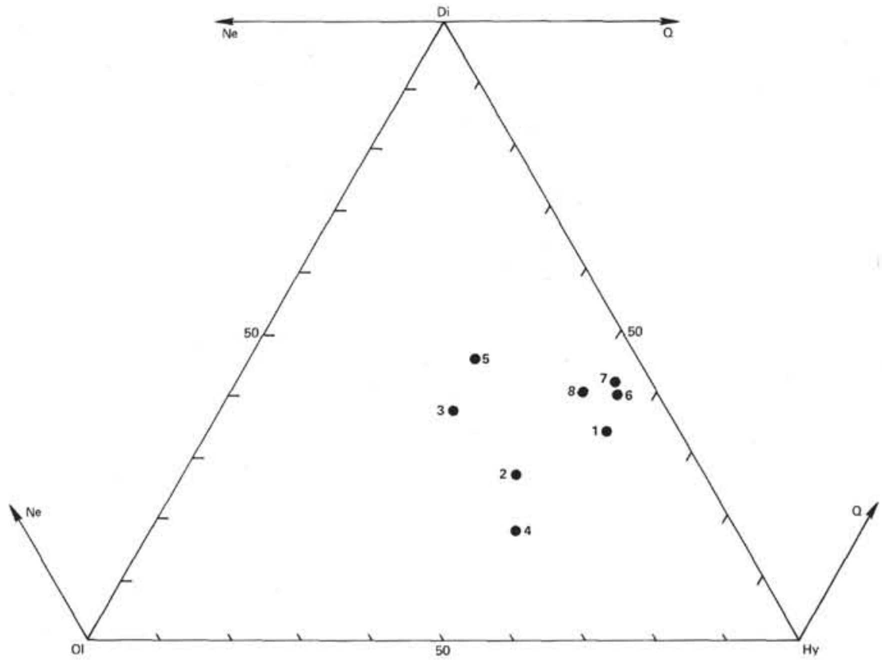

Figure 4. *Ne-Di-Ol-Hy-Q-plot of Core 7 samples. (Sample numbers same as in Figure 1.)*

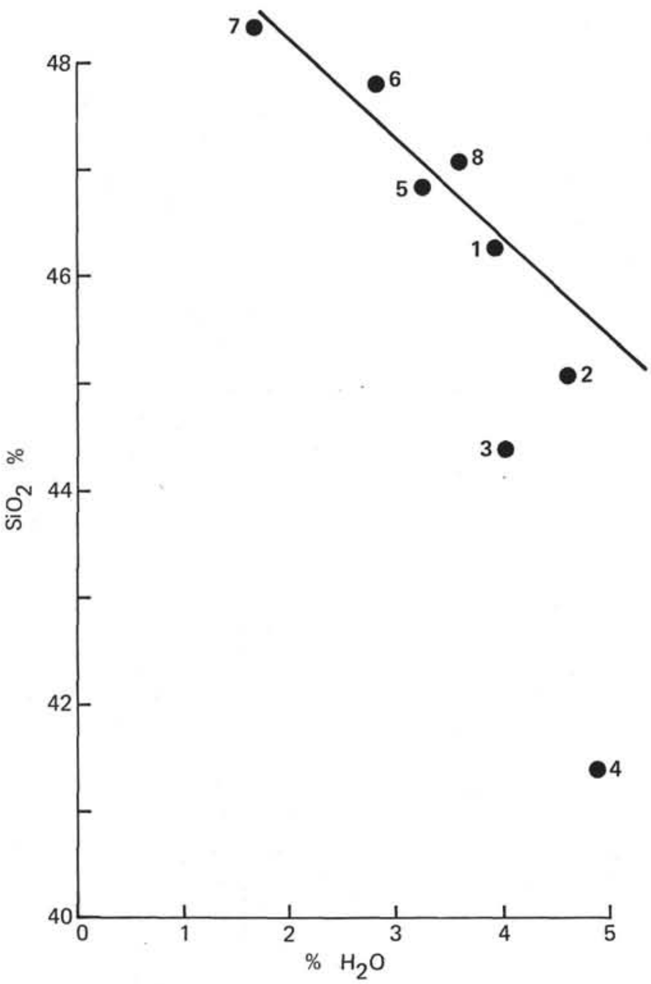

Figure 5. *SiO_2 – H_2O correlation of Core 7 basalt samples. (Sample numbers same as in Figure 1.)*

TABLE 5
K/Ar Data of Samples From Hole 373A, Core 7

Samples[a] (Interval in cm)	K[b] (%)	Radiogenic Argon (ccSTP/g) · 10^7	(%)	K/Ar-Age (m.y.)
7-2, 17-25	0.162	0.239 ± 0.047	4.9	3.7 ± 0.7
	0.167	0.315 ± 0.062	5.5	4.7 ± 0.9[c]
7-2, 34-41	0.205	0.282 ± 0.040	3.7	3.4 ± 0.5
	0.212	0.279 ± 0.095	2.7	3.3 ± 1.1[c]
7-2, 131-136	0.161	0.279 ± 0.050	6.2	4.3 ± 0.8
7-2, 142-150	0.143	0.287 ± 0.056	5.3	5.0 ± 1.0
7-4, 0-9	0.142	0.275 ± 0.054	5.0	4.9 ± 1.0
7-4, 74-83	0.156	0.224 ± 0.046	2.7	3.6 ± 0.8
7-4, 136-141	0.145	0.176 ± 0.039	10.6	3.0 ± 0.7
7-5, 0-7	0.247	0.35 ± 0.17	3.0	3.6 ± 1.7

Note: All errors given are intervals of 95% analytical confidence. For age calculations the constants of the "Phanerozoic Time Scale" (Harland and Francis, 1971) were used, i.e., $\lambda_\beta = 4.72\ 10^{-10}$ year^{-1}; $\lambda_e = 0.584\ 10^{-10}$ year^{-1}; $^{40}K/K = 1.19\ 10^{-2}$ atom %.

[a]Generally, whole rock ground to 400-250 μm, preheated overnight to <150°C except where noted.

[b]Relative analytical error of K analysis = ± 2%.

[c]Whole-rock fraction 800-400 μm, preheated overnight to <80°C.

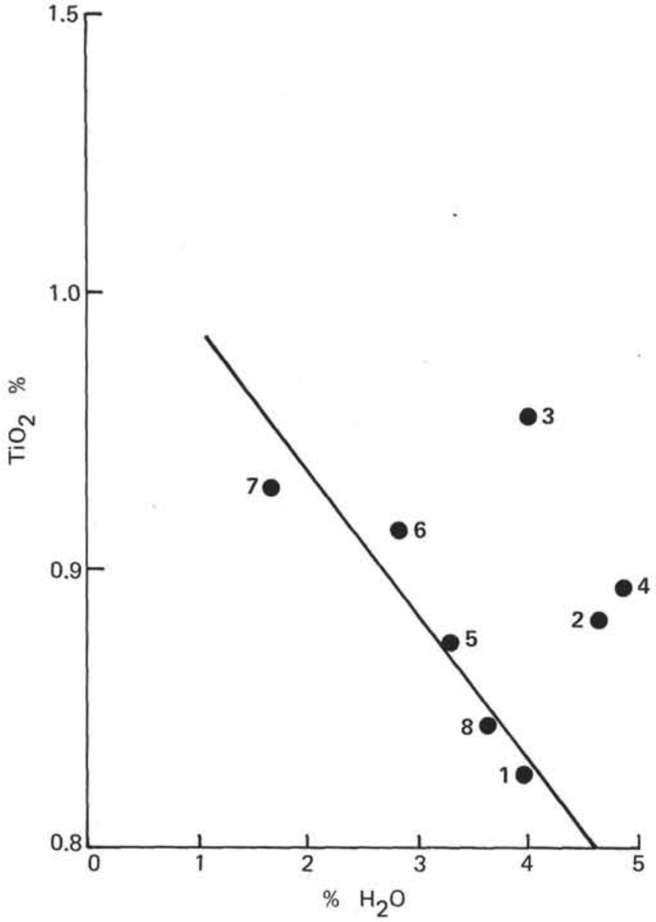

Figure 6. *TiO_2 - H_2O plot of Core 7 samples. (Sample numbers same as in Figure 1.)*

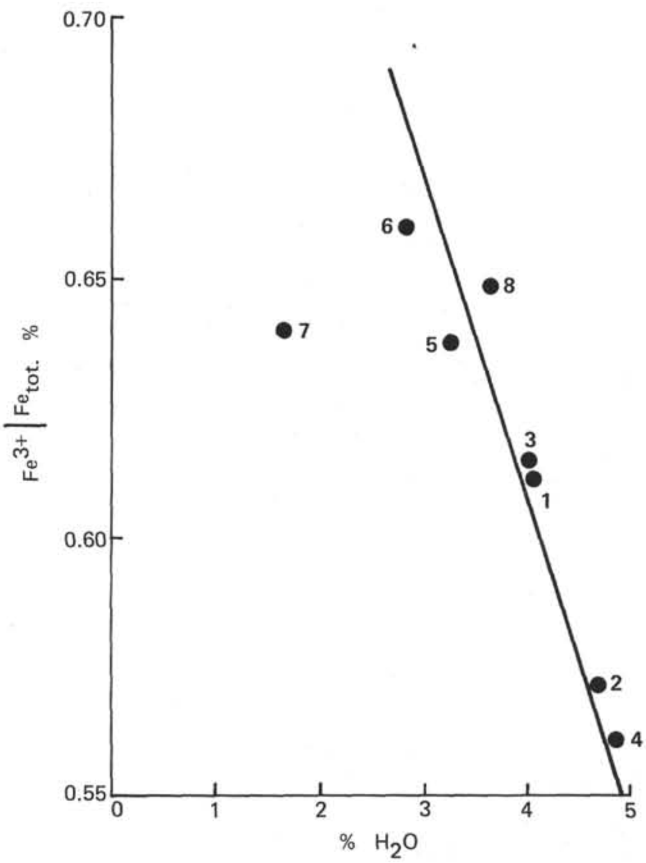

Figure 7. *Fe^{3+}/Fe_{total} vs. H_2O. (Sample numbers same as in Figure 1.)*

20.2. K/Ar AGE DETERMINATIONS ON BASALT ROCKS FROM HOLE 373A

C. Savelli and E. Lipparini, Laboratorio di Geologia Marina, CNR, Bologna, Italy

Three basalt rock specimens from Hole 373A were analyzed. Two are from lithologic Unit IV (Core 7, Section 2). Sample 1 (Table 1) was from the interval 67-76 cm and Sample 2 from 5-12 cm. The samples were chosen as being the freshest of a total of five samples from Core 7 at our disposal. Two other samples (from cores 12 and 4, respectively) are not analyzed because of obvious alteration. The basalt in the analyzed samples is porphyritic and has phenocrysts of plagioclase, "iddingsitized" olivine, and rare brown spinel in a groundmass consisting of plagioclase, pyroxene, olivine, ore, and alteration products (mainly those of glass, smectites, and limonite). Further, a secondary mineral is calcite, which fills some of the void spaces of the rock. Plagioclase and pyroxene crystals are fresh, as is shown in Figure 1.

The third specimen was from lithologic Unit V (Core 12, section 1, 120 cm; Sample 3 of Table 1). Its petrographic composition corresponds fairly well with the average composition of the whole unit as given above: plagioclase 45% to 60%, pyroxene 20% to 25%, and alteration minerals 20% to 30%. Plagioclase and pyroxene crystals are significantly altered as is shown in Figure 2.

For argon isotopic determinations high-frequency induction heating and an all-metal mass spectrometer were used. Samples were preheated in vacuum at about 160°C for 20 hr. Potassium was analyzed by