K–Ar dating by peak comparison method
—New technique applicable to rocks
younger than 0.5 Ma—

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Abstract: K–Ar dating for the samples younger than 0.5 Ma has been improved. In this new method, radiogenic ^{40}Ar was determined by the peak comparison method with a new mass spectrometer and potassium by the flame emission spectrometry, in which lithium internal standard and peak integration were adopted.

In order to assure the accuracy and precision of this method, K–Ar dating was made on some Quaternary reference materials and samples with known ages which were in the order of 0.1 Ma. The K–Ar ages obtained were in a good agreement with the known values within the errors of about 5%.

Furthermore, the errors for K–Ar age were estimated for the "ideal basaltic rock" younger than 0.1 Ma. The result suggests that K–Ar age of the 0.05 Ma ideal basaltic rock can be determined within 15% error.

1. Introduction

Precise age determination of volcanic materials younger than about 0.5 Ma is one of the most important geochronological subjects to be realized. Even though K–Ar dating method is considered to be the most reliable one applicable for such young volcanics (DARLYMPLE, 1968; HALL and YORK, 1978; GILLOT et al., 1979, 1982; CASSIGNOL and GILLOT, 1982), there are a few serious problems to be solved in order to obtain meaningful geologic ages. Conventional K–Ar dating method presumes the initial argon isotopic ratios for all dated samples to be equal to that of the present atmosphere (DARLYMPLE and LANPHERE, 1969). This assumption becomes very questionable when very young volcanics are dated because radiogenic ^{40}Ar accumulated in them is very small and less than 10% of

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total ^{40}Ar. DARLYMPLE (1969) measured ^{40}Ar/^{36}Ar ratios of twenty-six historic subaerial volcanic rocks, and clarified that eighteen of them had ratios identical to the atmospheric one within analytical uncertainties, five of them had ratios higher and three of them had ratios lower than the atmospheric ratio. Except for the anomalous value of alkali basalt from Hualalai including abundant olivine megacrysts, the lavas having ^{40}Ar/^{36}Ar ratios different from the atmospheric argon gave apparent ages less than ±0.2 Ma. On the other hand, KRUMMENACHER (1970), KANEOKA (1980) and MATSUMOTO et al. (submitted) measured ^{38}Ar/^{36}Ar ratios of historic volcanic rocks in addition to ^{40}Ar/^{36}Ar ratios and clarified that some modern volcanic rocks have different argon isotopic ratios from that of the atmosphere, and that these values generally fall on the fractionation line of the atmospheric argon. If volcanic rocks had different ^{40}Ar/^{36}Ar ratios when they consolidated, we can not

obtain correct K–Ar ages by conventional method.

Recently, TAKAOKA *et al.* (1989) demonstrated the usefulness of the peak comparison method for dating volcanic rocks younger than about 0.5 Ma in comparison with the widely used isotope dilution method. The merit for the peak comparison method is that $^{38}Ar/^{36}Ar$ ratios of samples can also be measured. Therefore, we can know whether the initial argon isotopes were fractionated from the atmosphere by the $^{38}Ar/^{36}Ar$ ratio of samples measured and also correct the initial $^{40}Ar/^{36}Ar$ ratio of them, although there remains a possibility that such rocks might have excess ^{40}Ar. In this paper, we describe the K–Ar dating technique using the peak comparison method for our new mass spectrometer, and discuss the usefulness for dating very young volcanic rocks younger than 0.5 Ma.

2. Principle

K–Ar dating is based on the fact that ^{40}K decays to ^{40}Ar or ^{40}Ca with a half life of 1.25×10^9 years (STEIGER and JÄGER, 1977). K–Ar age can be calculated by the equation (1), when concentrations of ^{40}K and radiogenic ^{40}Ar in samples have been known.

$$t = \frac{1}{(\lambda_e + \lambda_\beta)} \ln \left[\frac{^{40}Ar_{(rad.)}}{^{40}K} \left(\frac{\lambda_e + \lambda_\beta}{\lambda_e} \right) + 1 \right] \quad (1)$$

t   : K–Ar age
λ_e : Decay constant from ^{40}K to ^{40}Ar $(0.581 \times 10^{-10}/y)$
λ_β : Decay constant from ^{40}K to ^{40}Ca $(4.962 \times 10^{-10}/y)$
$^{40}Ar_{(rad.)}$: Concentration of radiogenic ^{40}Ar
^{40}K : Concentration of ^{40}K

It is assumed that the present–day atomic abundance ratio of ^{40}K to total potassium in terrestrial rocks and minerals is constant to be 1.167×10^{-4} (STEIGER and JÄGER, 1977). Then, the concentration of

^{40}K can be calculated from the total potassium concentration. On the other hand, the concentration of radiogenic ^{40}Ar is obtained by the isotopic analysis of argon, because the abundance ratio of radiogenic ^{40}Ar to total argon varies in each sample.

In this study, the radiogenic ^{40}Ar is determined by the peak comparison method (TAKAOKA *et al.*, 1989). The concentration of total ^{40}Ar in a sample is obtained by the comparison of peak intensity with the known amount of air standard. Then, the concentration of radiogenic ^{40}Ar is calculated by the equation (2).

$$^{40}Ar_{(rad.)} = {}^{40}Ar_{(total)} (1 - R_0/R) \quad (2)$$

$^{40}Ar_{(total)}$: Concentration of total ^{40}Ar in a sample
R_0 : Initial $^{40}Ar/^{36}Ar$ ratio
R : $^{40}Ar/^{36}Ar$ ratio in a sample

In the conventional K–Ar dating, the initial $^{40}Ar/^{36}Ar$ ratio in a sample is assumed to be equal to that of the present-day atmosphere. However, argon isotopic ratios in many historic lavas have been clarified to be mass fractionated from that in the present-day atmosphere (MATSUMOTO *et al.*, submitted). In this study, we estimated the initial $^{40}Ar/^{36}Ar$ ratio (R_0) in a sample on the assumption that the initial $^{40}Ar/^{36}Ar$ ratios in all volcanic rocks lie on the fractionation line from the present-day atmosphere, as shown in the equation (3) and (4).

$$\delta = (r/r_A - 1)/2 \quad (3)$$
$$R_0 = R_A (1 + 4\delta) \quad (4)$$

R_0 : Estimated initial $^{40}Ar/^{36}Ar$ ratio in a sample
R_A : $^{40}Ar/^{36}Ar$ ratio in the present-day atmosphere
r_A : $^{38}Ar/^{36}Ar$ ratio in the present-day atmosphere
r : $^{38}Ar/^{36}Ar$ ratio in a sample

As is clear from the above equations, the initial $^{40}Ar/^{36}Ar$ ratio (R_0) should be equal to the atmospheric value (R_A), if the $^{38}Ar/^{36}Ar$ ratio in a sample is equal to that of the

atmosphere.

The uncertainty for age determinations by the peak comparison method is calculated by the equation (5)–(7). These equations are introduced by the application of "law of propagation of errors" into the equation (1)–(4).

$$\sigma_T{}^2 = \sigma_K{}^2 + \sigma_{Ar}{}^2 \qquad (5)$$

$$\sigma_{Ar}{}^2 = \left[\sigma_X{}^2 + \frac{A_c{}^2}{(1-A_c)^2}(\sigma_R{}^2 + \sigma_{R0}{}^2) \right] \qquad (6)$$

$$\sigma_{R0} = [2r\sigma_r / (2r - r_A)] \qquad (7)$$

$$A_c = [(2r - r_A)R_A / r_A R] \qquad (8)$$

σ_T : Error for K–Ar age

σ_K : Error for determination of potassium

σ_{Ar}: Error for determination of radiogenic ^{40}Ar

σ_X : Error for determination of total ^{40}Ar

σ_R : Error for determination of $^{40}Ar/^{36}Ar$ ratio

σ_{R0}: Error for initial $^{40}Ar/^{36}Ar$

σ_r : Error for determination of $^{38}Ar/^{36}Ar$ ratio

A_c : Fraction of atmospheric argon

The estimation of σ_K, σ_X, σ_R and σ_r will be discussed later.

3. Apparatus

The system for determination of argon isotopic ratios consists of mass spectrometer, extraction furnace and purification system. Most of them are made of stainless steel. Each system is connected by high vacuum metal valves and ICF flanges sealed with copper gaskets.

3.1 Mass spectrometer

A VG Isotopes 1200C mass spectrometer is used in this work; its layout is shown in Fig. 1. This mass spectrometer uses a Nier type ion source. The electro-magnetic analyser has a 120 mm radius and a 60° deflection. The detector provides a Faraday cup (the head amplifier is equipped with a $10^{11}\,\Omega$ resister) and an electron multiplier. The resolution is better than 170, when a Faraday cup is used. The adjustment of magnet current, the finding of
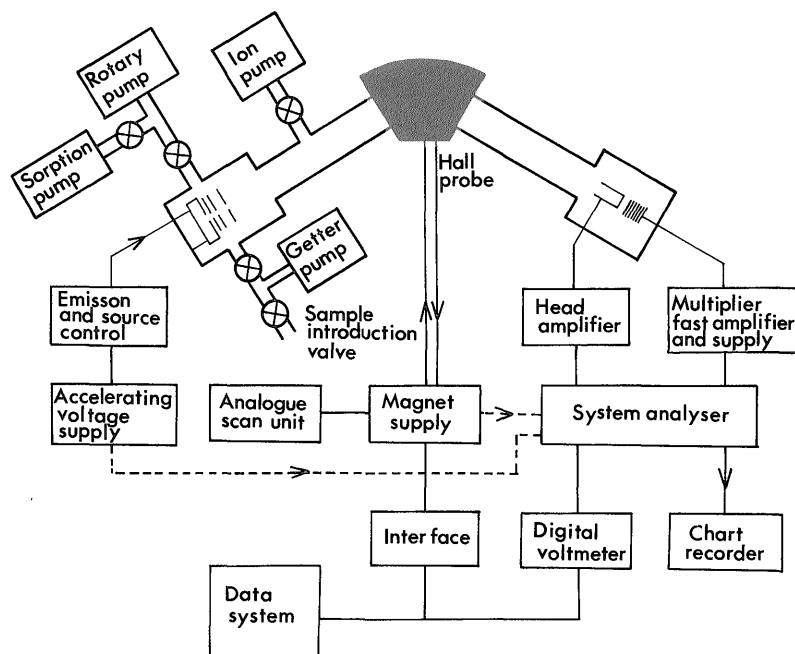

Fig. 1   Layout of masspectrometer (VG Isotopes 1200C).

peak centers for each argon isotope, and the integrations of peak and base line intensities are controlled by a personal computer through the system analyser. At the normal operation, the vacuum is kept at less than 2×10^{-9} mbar with a 30 l/s ion pump.

3.2 Extraction furnace

The extraction of argon is done with a tantalum resistance furnace originally designed by Professor Takaoka of Yamagata University. Although the basic specification of the furnace is the same as that of NAGAO and ITAYA (1988), the heating operation of our furnace is controlled automatically. The temperature of the molybdenum crucible is always measured by the controller and the output of this furnace is stabilized at the pre-set temperature.

3.3 Argon purification system

The extracted argon is purified with the rare gas purification system prepared by VG Isotopes. The outline is shown in Fig. 2. The U–shaped cold trap, which is soaked

in the ethanol cooled down to melting point with liquid nitrogen, traps mainly water. Active gases are adsorbed on two Zr–Ti alloy getter pumps, i.e., nitrogen, oxygen and hydrocarbons on the getter pump (G.P.1) heated at 250°C, while hydrogen on that (G.P.2) kept at room temperature. The purified argon is collected on the charcoal trap (C.T.) cooled down with liquid nitrogen. The part A in the purification system (Fig. 2) is usually pumped with a 30 l/s ion pump, while the part B and the extraction furnace are pumped with an oil diffusion pump equipped with a liquid nitrogen trap. The vacuum in each part is kept at less than 1×10^{-8} mbar.

4. Experiment

4.1 Preparation of samples

1–3 g of a sample was wrapped in a 10 μm thick copper foil and was loaded in the X'mas-tree type sample holder, as shown in Fig. 3 (twelve samples can be loaded). This holder was fixed at the top of the ex-
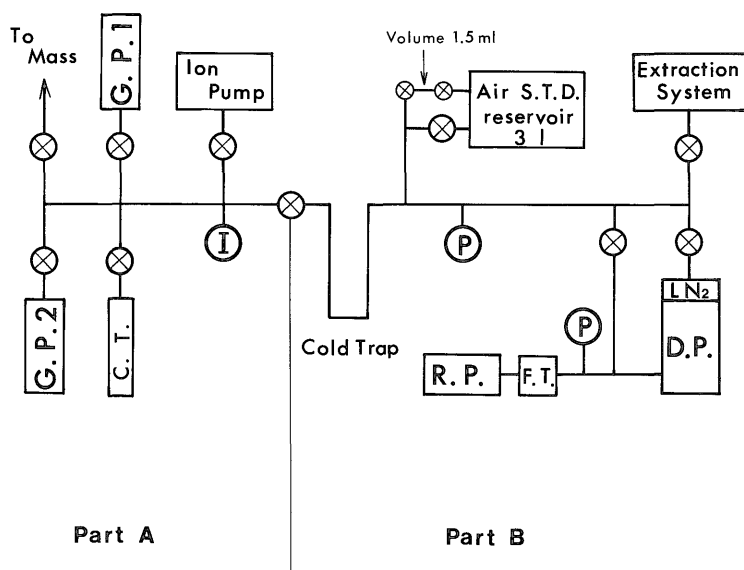

Fig. 2 Outline of argon purification system.
R.P.: Rotary pump, D. P.: Oil diffusion pump, F.T.: Foreline trap, LN2: Liquid nitrogen trap, ⊗: Metal valve, C.T.: Charcoal trap, ①: Ion gauge, Ⓟ: Pirani gauge, G.P.1: Zr–Ti alloy getter pump (heated at 250°C), G.P.2: Zr–Ti alloy getter pump (kept at room temperature).

traction furnace and was preheated with a flexible heater at 125°C for 48–72 hours until the pressure in the extraction furnace became less than 5×10^{-8} mbar. During the preheating of samples, the molybdenum crucible was heated twice in order to degass at 1500°C for 30 minutes. The purification line was also heated at 150°C for 3 hours by flexible heaters at the beginning and the end of the preheating of samples in order to remove gasses adsorbed on the wall of the line.

4.2 Extraction and purification of argon

The sample was dropped into the crucible by moving an iron chip in the sample holder with magnets. Most of samples were heated up to 1500°C by 30 minutes and kept at 1500°C for 15 minutes to be melted completely, though the heating speed and maximum temperature was slightly modified on the special samples. During this procedure, the gases extracted were purified with the U–shaped cold trap and the two Zr–Ti alloy getter pumps, and purified argon was collected on the charcoal trap cooled down with liquid nitrogen. The pressure of purified argon was monitored with an ion gauge before introduction to the mass spectrometer. If the
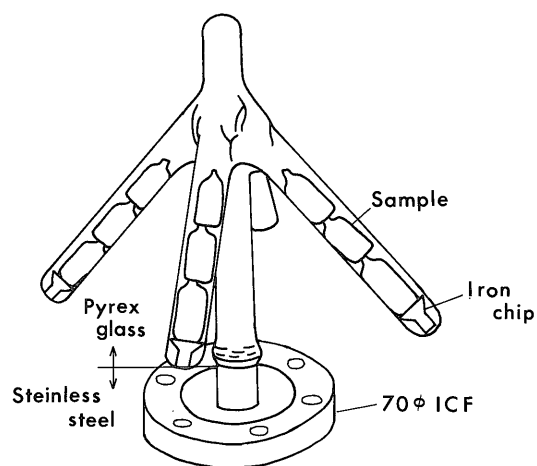
amount of argon exceeded the upper detection limit of the mass spectrometer, it was diluted with valve operations.

These Zr–Ti alloy getter pumps can be used more than five times in the purification of 1 g each of samples without refreshment. The Zr–Ti alloy getter pumps was refreshed by heating up to 750°C for 50 minutes under pumping with an diffusion pump. During the refreshment, the purification line was also preheated at 200°C with flexible heaters.

4.3 Measurement of argon isotopic ratios

The purified argon was introduced to the mass spectrometer and the intensity of argon isotopes were measured nine times in the condition shown in Tables 1 and 2. The magnet current for each argon isotope had been memorized into a personal computer by a program "Mass calibration" using the air standard. The magnet current

Fig. 3 Sample holder.

Table 1 Determination condition for argon isotopic ratios.

Ion accelerating voltage	4.02 KV
Filament current	2.55 A
Trap current	230 μA
Emission current	1.5 mA
Repeller voltage	-6.85 V
Magnet current	2.10–2.20 A
Slit width	0.5 mm
Collector	Faraday cup

Table 2 Program for measurement of argon isotopes.

No.	Mass No.	Integration time (sec.)	Comment
1	35.568	4 (10)*	baseline for ^{36}Ar
2	35.968	7 (10)	^{36}Ar peak
3	36.468	4 (10)	baseline for ^{36}Ar and ^{38}Ar
4	37.963	12 (15)	^{38}Ar peak
5	38.463	4 (15)	baseline for ^{38}Ar and ^{40}Ar
6	39.962	4	^{40}Ar peak

* Numbers in parenthesis are integration time of blank measurement.

corresponding to the center of ^{40}Ar peak was also measured at the beginning of sample measurement to correct fine drift of magnet current. The sensitivity of the mass spectrometer in this condition was 4.3×10^{-8} ml STP Ar/V.

4.4 Calibration of air standard

The amount of argon in air introduced from the air standard reservoir by the operation of pipettes, was measured by the following procedure. The weight of standard material (JG–1 biotite) used was 0.017–0.020 g.

(a) Argon in JG–1 biotite was extracted and purified by the procedure mentioned in 4.2. Then, ^{40}Ar intensity and ^{40}Ar/^{36}Ar ratio were determined with the mass spectrometer.

(b) The air introduced from the reservoir was also purified by the same procedure as (1). Then, ^{40}Ar intensity and ^{40}Ar/^{36}Ar ratio were determined.

(c) The sensitivity of the mass spectrometer at that time (ml STP/V) was calculated with the concentration of radiogenic ^{40}Ar in JG–1 biotite (2.49×10^{-5} ml STP/g; UCHIUMI and SHIBATA, 1980), and with the ^{40}Ar intensity (V/g) and ^{40}Ar/^{36}Ar ratio in JG–1 biotite determined in (a).

(d) The amount of ^{40}Ar in air introduced from the reservoir was calculated with the sensitivity obtained in (c) and the ^{40}Ar intensity in air determined in (b). The depletion of air standard in the reservoir was corrected with the equation (9) and (10).

$$\delta = V_T / (V_P + V_T) \qquad (9)$$
$$\text{Air}_{(t)} = \text{Air}_{(i)} \delta^{(t-1)} \qquad (10)$$

V_P : Volume of pipettes (1.5 ml)
V_T : Volume of reservoir (3 l)
t : The number of times used
$\text{Air}_{(i)}$: The initial amount of air introduced from the reservoir
$\text{Air}_{(t)}$: The amount of air at the t–th introduction

4.5 Determination of potassium

The sample for determination of argon isotopic ratios was further ground with an agate mortar. 0.1–0.2 g of this sample was decomposed with HNO_3, HF and $HClO_4$. Finally, concentration of potassium was determined by the flame emission spectrometry, in which lithium internal standard and peak integration were adopted (MATSUMOTO, 1989).

5. System blank analysis

For the accurate determination of radiogenic ^{40}Ar in samples, it is necessary to correct system blanks on sample analyses. Blank measurements are described as follows and the influence of blanks on the sample analyses is evaluated.

5.1 Cold blank (blank from the mass spectrometer itself)

The background output profile scanned at around the mass number 35 to 40 in the static condition is shown in Fig. 4. There are two distinct peaks at the mass number 35 and 37, and also two trace peaks at 36 and 38. As both intensity ratios are about 3:1, this implies that the distinct peaks are derived from ^{35}Cl and ^{37}Cl, and that two trace peaks at 36 and 38 may also be derived from ^{1}H^{35}Cl and ^{1}H^{37}Cl which are formed by the combination of hydrogen with chlorine. It would be important to correct them on sample analyses, because ^{36}Ar and ^{38}Ar can not be separated from ^{1}H^{35}Cl and ^{1}H^{37}Cl, respectively, for the current resolution of this mass spectrometer (170). Although a distinct peak by the memory effect of ^{40}Ar (about 3.5×10^{-11} ml STP) is also observed, it is negligible compared with ^{40}Ar in samples, because ^{40}Ar in cold blank is less than 0.04% of that in samples.

5.2 Hot blank

During heating and purification procedure of samples, argon and other gasses come from the crucible and the wall of lines in addition to gasses released from sample
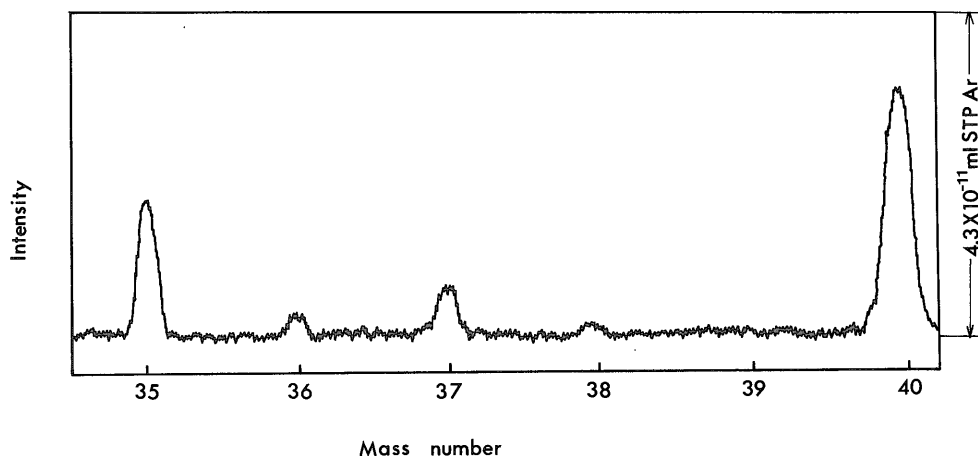
Fig. 4 Mass spectrometer background around mass number 35–40 in static condition.

itself. Such background gases released from the crucible and the wall of lines added to cold blank is so called "hot blank". In order to subtract the hot blank, argon measurements in the empty condition are always done with the same extraction procedure as actual sample analyses before sample introduction. The amount of hot blank is in the range of 0.2–1.0×10^{-8} ml STP ^{40}Ar and it tends to be large when a new crucible is used and/or many samples remain in the sample holder. ^{38}Ar/^{36}Ar and ^{40}Ar/^{36}Ar ratios in hot blank are within 0.198–0.234 and 222–279, respectively. There is also the tendency that ^{38}Ar/^{36}Ar and ^{40}Ar/^{36}Ar ratios approach the atmospheric value with the increase of hot blank. This may imply that the influence of cold blank (the apparent ^{38}Ar/^{36}Ar $\fallingdotseq 0.33$ and ^{40}Ar/^{36}Ar $\fallingdotseq 12$) in hot blank relatively decreases with the increase of the atmospheric argon released from the crucible, samples remained in the sample holder and the lines during the extraction and purification.

5.3 Blank of metal foils

The metal foil for wrapping crushed samples should have lower melting point than that of samples and have low argon blank. Argon blanks in copper, tin and aluminum foil (10μm thick), which are commercially available, were determined. The result is shown in Table 3. As the blank in copper foil is the lowest, samples are wrapped in copper foil in this work. The blank from copper foil in the extraction of 1 g sample is estimated to be 1.7×10^{-10} ml STP, because about 0.18 g of copper foil is necessary to wrap 1 g each of samples.

5.4 Effect of blank on sample analyses

The influence of these blanks on sample analyses was evaluated with the means of cold blank, hot blank and copper foil blank shown in Table 4. The copper foil blank is negligible because it is about 3% of hot blank, and cold blank is included in hot blank. Therefore, only hot blank is considered for correction of system blanks. The fraction of hot blank to the amount of ^{40}Ar introduced to the mass spectrometer

Table 3 Argon blank in metal foils (10μm thick).

Sample	^{40}Ar blank (ml STP/g)
Al	3.0×10^{-7}
Sn	4.9×10^{-8}
Cu	9.7×10^{-10}

Table 4 The influence of blanks on sample analyses.

Ar isotope	Cold blank (ml STP)	Hot blank (ml STP)	Cu foil blank* (ml STP)
^{36}Ar	3×10^{-12}	2.5×10^{-11}	$<5 \times 10^{-13}$
^{38}Ar	1×10^{-12}	5.4×10^{-12}	$<2 \times 10^{-13}$
^{40}Ar	3.5×10^{-11}	6.5×10^{-9}	1.7×10^{-10}

* Cu foil blank is given by the blank in 0.18 g of Cu foil, necessary to wrap 1 g of sample.
Only hot blank is considered for correction of system blanks, because Cu foil blank is 3% of hot blank and cold blank is included in hot blank.

is 7.6, 3.0 and 1.5% in 0.86, 2.2 and 4.3×10^{-7} ml STP ^{40}Ar, respectively. The correction of hot blank is important especially for the samples having lower concentration of argon. Hot blank is always measured before actual sample analyses and its value is subtracted from argon concentration of the samples.

6. Air standard analysis

In the peak comparison method, the concentration of radiogenic ^{40}Ar in a sample is obtained by the comparison of peak intensity with a known amount of air standard. Therefore, a long-term stability of the mass spectrometer and a linearity between the amount of argon and the peak intensity should be confirmed, and then the amount of ^{40}Ar in air introduced from the reservoir also should be calibrated.

6.1 Stability of mass spectrometer

A long-term stability of the mass spectrometer was evaluated by measuring ^{40}Ar intensity, $^{38}Ar/^{36}Ar$ and $^{40}Ar/^{36}Ar$ ratios of the air standard for three months. Table 5 shows the result of the thirty-seven analyses during three months. $^{38}Ar/^{36}Ar$ and $^{40}Ar/^{36}Ar$ ratios are determined with good precisions ($^{38}Ar/^{36}Ar = 0.1893 \pm 0.0005$ and $^{40}Ar/^{36}Ar = 296.7 \pm 0.6$) and these ratios are somewhat discriminated from the known atmospheric value ($^{38}Ar/^{36}Ar = 0.1869$ and $^{40}Ar/^{36}Ar = 295.5$; NIER, 1950). In the acutual samples analyses, the mass discrimination is corrected with the argon isotopic ratios of the air standard measured and those of NIER (1950). The variation of sensitivity for argon is estimated about 3%, because the standard deviation for ^{40}Ar intensity of the air standard 3.4% during three months.

6.2 Linearity between the amount of argon and the peak intensity

The linearity between the amount of argon introduced to the mass spectrometer and the argon intensity was evaluated by varying the amount of ^{40}Ar introduced to 1/3, 1/2 and 1.5 times as much as that in 6.1. The result shown in Fig. 5 indicates that there is a good linearity of the argon intensity in this range, because the regression coefficient between the amount of Ar and the ^{40}Ar intensity is 0.999.

6.3 Calibration of air standard

The amount of ^{40}Ar in air introduced from the air standard reservoir was calibrated by the procedure mentioned in 4.4 using JG–1 biotite. In this calibration, hot blank, mass discrimination and depletion of air standard in the reservoir were corrected. The result is shown in Table 6.

Table 5 Reproducibility of air standard analyses.

$^{38}Ar/^{36}Ar$	$^{40}Ar/^{36}Ar$	^{40}Ar intensity* (V)	Times
0.1893 ± 0.0005	296.7 ± 0.6	8.013 ± 0.275	37
(C.V. 0.26%)	(C.V. 0.13%)	(C.V. 3.43%)	

* The depletion of air standard in the reservoir is corrected.
^{40}Ar introduced to the mass spectrometer is 3.44×10^{-7} ml STP.
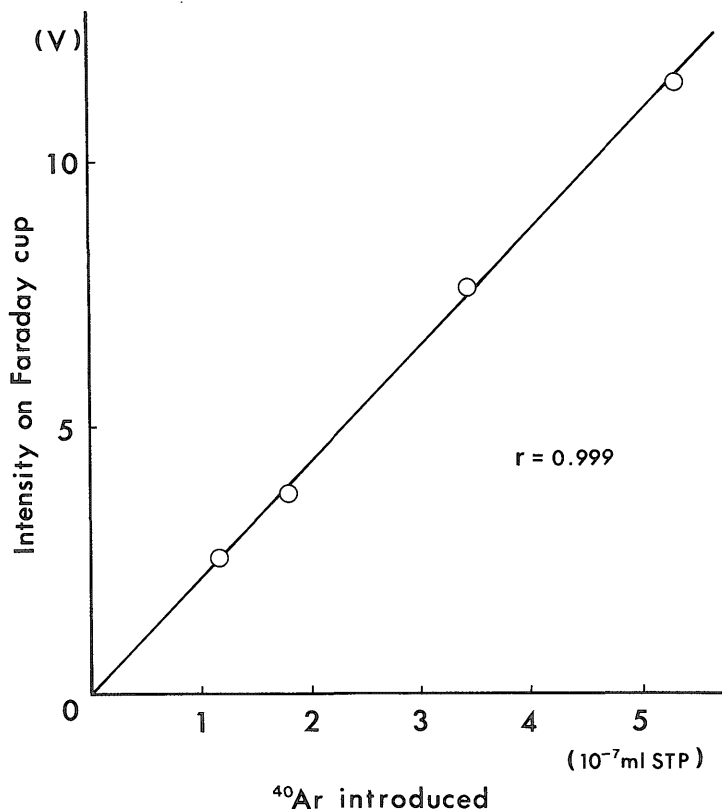
Fig. 5   Linearity between the amount of argon and the peak intensity.

The mean of eight calibrations is 3.44×10^{-7} ml STP and the standard deviation is 1.7%. In the following determination of radiogenic ^{40}Ar, the sensitivity of the mass spectrometer for argon at that time is calculated with this value $(3.44 \times 10^{-7}$ ml STP) and ^{40}Ar intensity of the air standard.

Table 6   Calibration of ^{40}Ar in air standard using JG–1 biotite.

^{40}Ar in the air standard $(10^{-7}$ ml STP)			
3.487	3.529	3.408	3.453
3.337	3.412	3.462	3.422
Average	3.44 ± 0.06		
	(C.V. 1.7%)		

7.   Error estimation

The estimation of errors $(\sigma_K, \sigma_X, \sigma_R, \sigma_r)$, which are necessary for the calculation of error for K–Ar age, is done as follows.

7.1 σ_K (error for determination of potassium)

The replicate determinations of potassium made on the samples for K–Ar dating indicate the standard deviations of less than 0.5%. σ_K, therefore, is estimated to be 0.5%.

7.2 σ_X (error for determination of total ^{40}Ar)

σ_X is estimated to be 4% from the following results : the standard deviation in the calibration of air standard is 1.7%, the variation of ^{40}Ar intensity during three months is 3.4% and the error for ^{40}Ar intensity in each measurement is about 0.1%.

7.3 σ_R and σ_r (error for determination of $^{40}Ar/^{36}Ar$ and $^{38}Ar/^{36}Ar$ ratio)

In the estimation of σ_R and σ_r, not only the errors for the determination of $^{38}Ar/^{36}Ar$ and $^{40}Ar/^{36}Ar$ ratios in samples, but also the errors produced in the correction for hot blank and mass discrimination of the mass spectrometer are considered. σ_R and σ_r in the determination of samples younger than 0.5 Ma is usually less than 0.23% and 0.45%, respectively.

8. Age determination on reference materials

The accuracy and precision of our K–Ar dating were checked with the following reference materials, in which hot blank and mass discrimination were corrected.

8.1 Bern 4B

Bern 4B is a well-known reference material for conventional K–Ar dating of Bern University and the concentration of radiogenic ^{40}Ar is recommended to be 5.33×10^{-6} ml STP/g (FLISH, 1982). K–Ar age was determined independently four times and the results are shown in Table 7. As the fraction of atmospheric argon in the sample is less than 20%, the standard deviation for determination of $^{38}Ar/^{36}Ar$ ratio (σ_r) is considerably large as 0.7–1.2%. However, when the fraction of atmospheric argon is low, σ_r and the error for determination of $^{40}Ar/^{36}Ar$ ratio (σ_R) can be negligible compared with the error for determination of total ^{40}Ar (σ_X) from the equation (6)–(8). Therefore, the concentration of radiogenic ^{40}Ar in each determination can be obtained within 4% error and the mean is in an agreement with FLISH (1982).

8.2 BB–6 and YZ–1

BB–6 is the Quaternary reference material for K–Ar dating of Bern University and YZ–1 is that of Yamagata University. The K–Ar ages of BB–6 and YZ–1 are 0.441 ± 0.013 Ma (JÄGER et al., 1985) and 0.219 ± 0.008 Ma (N. TAKAOKA, PERSONAL COMMUNICATIONS), respectively. Four in-

Table 7   K–Ar ages of the reference materials (Bern 4B, BB–6 and YZ–1).

Sample Name	Sample wt. (g)	K_2O (%)	$^{38}Ar/^{36}Ar$	$^{40}Ar/^{36}Ar$	Atm. ^{40}Ar (%)	$^{40}Ar_{(rad)}$ (10^{-8} ml STP/g)	Age (Ma)
Bern 4B	0.06671		0.1859 ± 0.0020	1953 ± 10	15.0	502 ± 20	16.4 ± 0.7
	0.06562		0.1863 ± 0.0022	2000 ± 10	14.7	523 ± 21	17.1 ± 0.7
	0.06865	9.47 ± 0.02	0.1867 ± 0.0017	1411 ± 7	20.9	530 ± 21	17.3 ± 0.7
	0.06564		0.1872 ± 0.0014	1836 ± 4	16.1	507 ± 20	16.6 ± 0.7
					AV.	515 ± 10	16.9 ± 0.3
		9.53*				533*	
BB–6	2.0290		0.1866 ± 0.0010	388.0 ± 1.5	75.9	2.95 ± 0.16	0.451 ± 0.025
	3.0171	2.018 ± 0.009	0.1864 ± 0.0006	407.2 ± 0.7	72.2	2.81 ± 0.12	0.430 ± 0.019
	2.9941		0.1868 ± 0.0008	403.6 ± 0.8	73.1	2.87 ± 0.13	0.440 ± 0.021
					Av.	2.86 ± 0.08	0.438 ± 0.012
		2.02 ± 0.04**				2.884 ± 0.076**	0.441 ± 0.013**
YZ–1	1.0186		0.1873 ± 0.0033	371.1 ± 1.5	80.0	1.22 ± 0.18	0.223 ± 0.033
	3.0018	1.698 ± 0.005	0.1869 ± 0.0006	368.0 ± 0.8	80.3	1.19 ± 0.06	0.217 ± 0.010
	3.0247		0.1866 ± 0.0008	375.9 ± 0.9	78.4	1.22 ± 0.06	0.222 ± 0.012
					Av.	1.20 ± 0.04	0.219 ± 0.008
		1.70***				1.14 ± 0.07***	

Atm.^{40}Ar is the fraction of atmospheric ^{40}Ar. $^{40}Ar_{(rad)}$ is the concentration of radiogenic ^{40}Ar. The means are given by a weighted mean. *FLISH (1982), **JÄGER et al. (1985), *** N. TAKAOKA (PERSONAL COMMUNICATIONS)

dependent determinations of potassium and three of radiogenic ^{40}Ar were carried out on each sample. The results are shown in Table 7. σ_r can be determined within 0.45% and the error for K–Ar age (σ_T) is about 5% when the weight of sample is 3 g for the determination of radiogenic ^{40}Ar. From the equation (6)–(8), σ_r has the largest effect on σ_T in such samples as the fraction of atmospheric Ar is high. It is, therefore, necessary to increase the weight of sample in order to obtain a good precision in ^{38}Ar/^{36}Ar ratio and thus to reduce σ_T. The results in Table 7 show that more than 4.5×10^{-10} ml STP ^{36}Ar is necessary to determine ^{38}Ar/^{36}Ar ratio within 0.45% and that the concentration of radiogenic ^{40}Ar and K–Ar age in each sample are in a good agreement with JÄGER et al. (1985) and N. TAKAOKA (PERSONAL COMMUNICATIONS).

9. K–Ar dating of some age known samples

In order to check the accuracy of our method, K–Ar dating was further made on the samples whose K–Ar ages have been reported.

9.1 Fish Canyon Tuff biotite

Fish Canyon Tuff in southwestern U.S.A. is well dated both by K–Ar and fission–track methods and its age is 27.4 ± 0.41 Ma (HURFORD and HAMMERSCHMIDT, 1985). Zircon and apatite crystals separated from this tuff have become widely distributed standards for fission-track method. The biotite separated by us from the sample collected at the same outcrop as used for fission-track standard, was dated for the comparison.

The K–Ar age of Fish Canyon Tuff biotite is given in Table 8. Although this sample contains the same order of radiogenic and atmospheric ^{40}Ar as Bern 4B and σ_r is also considerably large as 0.8–1.3%, the K–Ar age in each determination

can be obtained within 4% error and the mean is in a good agreement with HURFORD and HAMMERSCHMIDT (1985).

9.2 Quaternary volcanic rocks from U.S.A.

Two Quaternary volcanic rocks (82C836 and 75ALC–17) in the order of 0.1 Ma were provided by Dr. Lanphere of U.S. Geological Survey. The K–Ar ages of them are shown in Table 8. The K–Ar age of 82C836 can be determined within 5% error when the weight of samples for the determination of radiogenic ^{40}Ar is 3 g, and it is in a good agreement with M. A. LANPHERE (PERSONAL COMMUNICATIONS) within the range of error. Although the K–Ar age of 75ALC–17 also can be determined within 4% error when the weight of sample for radiogenic ^{40}Ar is 3 g, it is about 10% younger than M. A. LANPHERE (PERSONAL COMMUNICATIONS). Nevertheless, it can not be necessarily concluded that there is a significant difference between M. A. LANPHERE (PERSONAL COMMUNICATIONS) and our result (0.573 ± 0.024 Ma), because his two K–Ar ages of this sample are 0.629 ± 0.040 and 0.639 ± 0.026 Ma.

9.3 Yugamine dacite

The K–Ar age of the dacite from Yugamine, Gero-cho, Gifu Prefecture (MATSUMOTO et al., in preparation) is shown in Table 8. The K–Ar age in each determination is in a good agreement with each other, the error of mean is less than 6% and the mean is in a good agreement with SHIMIZU et al. (1988). This result shows that K–Ar dating using the peak comparison method is reliable for young volcanic rocks of 0.1 Ma.

10. Possible age limit in the future

Samples in the order of 0.1 Ma were determined with a good accuracy and precision as shown in the previous sections. Then, the possible age limit by our method for the sample younger than 0.1 Ma is

Table 8 K–Ar ages of age known samples (Fish Canyon Tuff biotite, 83C836, 75ALCC–17 and Yugamine dacite).

Sample Name	Sample wt. (g)	K_2O (%)	$^{38}Ar/^{36}Ar$	$^{40}Ar/^{36}Ar$	Atm. ^{40}Ar (%)	$^{40}Ar_{(rad)}$ (10^{-8} ml STP/g)	Age (Ma)
	0.05536		0.1885±0.0016	2362± 8	12.7	792±32	27.6±1.1
Fish Canyon	0.05526		0.1860±0.0023	2439±10	12.0	772±31	26.9±1.1
Tuff biotite	0.06278	8.90±0.04	0.1867±0.0018	1830± 7	16.1	781±31	27.2±1.1
	0.06258		0.1861±0.0025	2563± 8	11.4	811±33	28.2±1.1
	0.06344		0.1863±0.0022	2306±11	12.7	796±32	27.7±1.1
					Av.	790±14	27.5±0.5
		8.92*				7.877*	27.15±0.37*
82C836	0.9994	1.511±0.005	0.1868±0.0017	370.5±1.1	79.7	1.84±0.15	0.377±0.031
	3.0277		0.1868±0.0006	364.3±0.6	81.0	1.74±0.09	0.356±0.018
					AV.	1.76±0.07	0.361±0.016
		1.529±0.003**				1.679**	0.341±0.008**
75ALe–17	1.0013	1.236±0.006	0.1867±0.0048	498.4±3.6	59.2	2.31±0.20	0.580±0.050
	3.0367		0.1869±0.0010	468.5±0.9	63.1	2.28±0.10	0.571±0.025
					AV.	2.28±0.09	0.573±0.022
		1.236±0.013**				2.519**	0.636±0.024**
Yugamine	0.2596		0.1866±0.0034	320.4±0.8	92.0	1.20±0.50	0.105±0.044
dacite	2.0397	3.548±0.010	0.1866±0.0007	321.3±0.8	91.7	1.16±0.11	0.102±0.010
	2.0493		0.1867±0.0005	321.6±0.6	91.7	1.17±0.09	0.102±0.008
					AV.	1.17±0.07	0.102±0.006
		3.59±0.18***			89.0***	1.42***	0.12±0.01***

The means are given by a weighted mean. *HURFORD and HAMMERSCHMIDT (1985), **M. A. LANPHERE, U.S.G.S. (PERSONAL COMMUNICATIONS), ***SHIMIZU *et al.* (1988)

estimated with the results of BB–6, YZ–1, 82C836, 75ALC–17 and Yugamine dacite, mentioned above. As the results suggest that σ_r and σ_R can be reduced to less than 0.45 and 0.23%, respectively, when the amount of ^{36}Ar introduced to the mass spectrometer is more than 4.5×10^{-10} ml STP, the possible age limit is estimated with these σ_r, σ_R, and $\sigma_k = 0.5\%$, $\sigma_X = 4\%$ mentioned in "Error estimation".

Generally, the concentration of atmospheric ^{40}Ar in basaltic samples is 0.5–1.5×10^{-7} ml STP/g and acidic rocks tend to have more atmospheric argon than basaltic ones. Figure 6 shows the relationship between concentration of K_2O and K–Ar age which can be determined in 10% error, when the concentration of atmospheric ^{40}Ar is 0.5 and 1.5×10^{-7} ml STP/g. From the figure, K–Ar age which can be determined within 10% error for the sample containing 2% of K_2O, is more than 0.079 and 0.24 Ma when the concentration of atmospheric ^{40}Ar is 0.5 and 1.5×10^{-7} ml STP/g, respectively. It also suggests that a younger age can be determined for the sample having lower fraction of atmospheric ^{40}Ar. On the other hand, when the concentration of atmospheric ^{40}Ar is the same, a younger age can be determined for the sample having higher potassium content.

Furthermore, the errors for K–Ar age of 0.01–0.1 Ma are estimated for the sample containing 0.5×10^{-7} ml STP/g of atmospheric ^{40}Ar and 2% of K_2O. The result is shown in Fig. 7. The concentration of atmospheric ^{40}Ar (0.5×10^{-7} ml STP/g) is nearly equal to the lower limit in basaltic
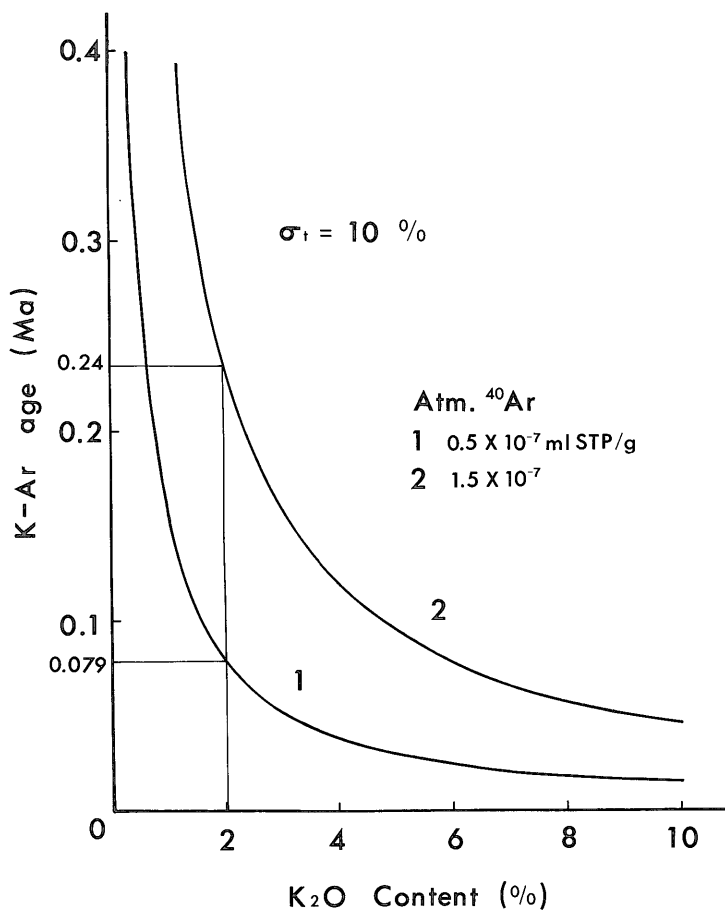
Fig. 6　Limit of K–Ar age within 10% error.
$\sigma_K = 0.5\%$, $\sigma_X = 4\%$, $\sigma_R = 0.23\%$, $\sigma_r = 0.45\%$

samples and K_2O (2%) is also to the upper limit. In other words, these values can be referred to the optimum condition for K–Ar dating of basaltic rocks. This figure suggests that the error in K–Ar age of the ideal basaltic rock at 0.05 Ma, which is the possible age limit in ^{14}C method (TOGASHI and MATSUMOTO, 1987), is about 15%. Therefore, the age gap of measurable limit between K–Ar and ^{14}C method is now eliminated in such an optimum condition. However, common basaltic rocks have more atmospheric ^{40}Ar and lower K_2O content than the ideal one. It would be most important to select the sample having lower atmospheric ^{40}Ar and higher K_2O content

in order to improve the precision in K–Ar dating of rocks younger than 0.1 Ma.

11.　Conclusion

K–Ar dating using the peak comparison method has been established. K–Ar dating for some reference materials and age known samples of 0.1–0.6 Ma, was carried out by this peak comparison method. The results are that K–Ar ages can be determined within 6% errors and are in a good agreement with the known values when the weight of samples is adjusted so as to introduce more than 4.5×10^{-10} ml STP of ^{36}Ar to the mass spectrometer.
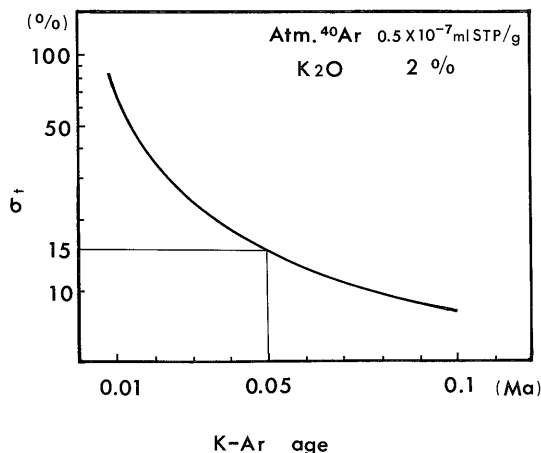
Fig. 7   Error of K–Ar age for the ideal basaltic sample.
σ_K=0.5%, σ_X=4%, σ_R=0.23%, σ_r=0.45%

There is no age gap of measurable limit between K–Ar and ^{14}C method in an ideal condition, because the error in K–Ar age of the ideal basaltic rock at 0.05 Ma, which is the possible age limit in ^{14}C method, can be estimated to be about 15%. Therefore, It is most important to select the sample having lower atmospheric ^{40}Ar and higher K_2O content in order to improve the precision in K–Ar dating of rocks younger than 0.1 Ma.

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ピーク値比較法による K–Ar 年代測定
―0.5 Ma より若い試料に対する新しい測定方法―

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要　旨

　50万年よりも若い試料に対する K–Ar 年代測定の精度および測定限界を向上させた．今回確立した測定方法では，試料中の放射性起源の ^{40}Ar 含量をピーク値比較法で求めた．このピーク値比較法とは，あらかじめアルゴンに対する質量分析計の感度を求めておき，その値と試料から抽出・精製したアルゴンの測定強度とその同位体比から放射性起源の ^{40}Ar 含量を求める方法であり，100万年より若い試料においては，従来用いられてきた同位体希釈法よりも測定精度が優れている．一方，カリウム含量についても，積分法とリチウム内部標準法を併用した炎光光度法によって測定精度および確度を向上させた．

　本法によって，数種の10万年オーダーの標準試料および年代が既に報告されている試料を測定したところ，得られた年代は，報告値と良く一致しており，また測定誤差も 5 ％程度であった．

　さらに10万年よりも若い玄武岩質試料について，本法による測定誤差を見積ったところ，玄武岩質試料における最適条件，すなわち，大気アルゴン含量の下限値とカリウム含量の上限値を満たした試料において，5 万年の試料を誤差15％程度で測定できる可能性があることが分かった．